TRINUCLEAR RUTHENIUM CARBOXYLATE COMPLEXES AS OXIDATION CATALYSTS

By

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KEY TO ABBREVIATIONS

Et_2O = diethyl ether

OAc = $CH_3CO_2^-$

pfb = $CF_3CF_2CF_2CO_2^-$

prop = $CH_3CH_2CO_2^-$

PPh_3 = triphenylphosphine

py = pyridine

tfa = trifluoroacetate

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The family of trinuclear metal carboxylate complexes has been known to chemists for over 100 years. General studies in terms of their classical inorganic chemistry, such as ligand exchange or electron transfer reactions and reactivity, are well documented in the literature. However, little application of this knowledge has been attempted.

The series of trinuclear ruthenium carboxylates is very intriguing in light of the extensive electrochemistry demonstrated in these complexes. The ready accessibility to a variety of oxidation states, combined with the facile exchange of ancillary ligands, should make these complexes ideal subjects for catalytic studies.

Previous work has shown a series of trinuclear ruthenium carboxylates $[Ru_3O(O_2CR)_6L_3]^n$ to be active catalysts for the oxidation of alcohols to carbonyl-containing products utilizing dioxygen as the primary oxidant. Continuation of this study has revealed a mechanism that utilizes the expected synergism between the metals in this cluster to explain the unique features of this oxidation.

A previously unknown member of this family, a complex containing completely fluorinated ligands, has been synthesized and characterized. Based on the accumulated evidence, this complex has been formulated as $[Ru_3O(O_2CCF_2CF_2CF_3)_6(Et_2O)_3](O_2CCF_2CF_2CF_3)$. This complex has been screened as a catalyst for a variety of organic transformations and has excelled in initiating the free radical autoxidation of several olefins again using dioxygen as the primary oxidant. The oxidation studies were extended to alkane oxidations as well, and were shown to occur by a slightly different mechanism than that assumed to operate in the industrial, cobalt-catalyzed oxidation of alkanes like cyclohexane.

CHAPTER I

GENERAL INTRODUCTION

Catalytic Oxidations

The oxidation of organic substrates as a field of interest to chemists has its origins in the beginnings of the history of chemistry as a science. Lavoisier, the father of modern chemistry, demolished the phlogiston theory when he explained the results of Priestley and Sheele's air experiments.[1] Air, he claimed, consisted of two parts, one of which will support combustion (Priestley's "fire gas") and one of which will not, and not "phlogiston." [2] He named the "fire gas" oxygen (for acid former) and formulated the theory of combustion in the late 1700s. In this origin the modern field of oxidation chemistry has its roots.

Detailed studies of oxidation processes began in the 1800s. The degradation of natural rubber was linked to oxygen absorption, and a great deal of research was aimed at discovering anti-oxidants for the rubber industry.[3,4] The modern theories of autoxidation processes (as the free radical oxidation of hydrocarbons by O_2 is known), were developed in the early 1900s. The effects of metal ions on this process were studied during this period by Haber and Weiss, who formulated the classical mechanism for metal-catalyzed autoxidation in use today.[3,4] (Figure 1.1)

$$In_2 \longrightarrow 2In\bullet$$

$$In\bullet + RH \longrightarrow R\bullet$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet$$

$$RO_2\bullet + RH \longrightarrow RO_2H + R\bullet$$

$$R\bullet + RO_2\bullet \longrightarrow RO_2R$$

$$2\ RO_2\bullet \longrightarrow RO_4R \longrightarrow \text{nonradical products}$$

Figure 1.1 Basic autoxidation pathways.[3,4]

Autoxidation as a means for producing oxygenated compounds from hydrocarbons is a highly desired process, although several serious flaws exist in present processes. Controlling the selectivity of an autoxidation process, a key element in terms of its usefulness, is extremely difficult due to the radical nature of the chemistry. A high activation energy, related to the spin-forbidden reaction between dioxygen (a triplet state) and organic molecules (a singlet state) is a barrier as well. Control of the process once initiated is another disadvantage--the reaction is often hard to stop short of CO_2 and H_2O.

Catalytic oxidations theoretically solve most of these problems in that the addition of a catalyst should lower the energy barrier, thus making the reaction easier to start. Product selectivity is drastically affected by the presence of a catalyst as well. For these reasons, the "Age of Petroleum" and the "Age of Catalysis" are inescapably linked.[3] Without catalysts to facilitate the conversion of crude oil to useful products, a petroleum-based economy would not be possible. Vice versa, without the widespread need for and use of chemicals and products derived from oil, the study of catalysis would be relegated to purely academic investigations. Sheldon and Kochi estimate that today over 90% of the organic chemicals in use are derived from petroleum, and the majority of petroleum and petrochemical processes involve the use of catalysts.[3] In terms of the importance of catalytic oxidations, industrial organic chemicals, including oxygenates from oxidative processes, made up 16.8% of the value of the total chemical industry in 1983.[5] Seven

of the top fifty chemicals (by volume) were produced directly from oxidation processes, and several others were produced from oxidatively generated intermediates.[5]

Obviously, catalytic oxidations are industrially valuable. Serious study and application of homogeneous, liquid-phase oxidation began in the 1950s.[3] Before this time, the majority of industrial processes used heterogeneous or supported catalysts. However, homogeneous catalyst systems offer several advantages, especially to the academician, over their heterogeneous counterparts. Generally milder reaction conditions (i.e., lower temperature and pressure) are used in homogeneous processes. Temperatures, mixing rates, and catalyst concentration are more effectively controlled, and most importantly, the reaction can feasibly be studied using standard spectroscopic methods. New, improved surface science techniques have made the study of heterogeneous catalysts easier, but the relative perspicuity inherent in homogeneous systems still outweighs these advances. The major disadvantages of homogeneous systems industrially are the difficulty in separating products from the reaction mixture and catalyst recovery. This last deterrent becomes a major problem when dealing with catalysts containing noble metals like rhodium or iridium due to their expense.

The advent of the Mid-Century Process (Equation 1-1) and the discovery of the Wacker process (Equation 1-2) heralded a widespread interest in homogeneous catalysis as well as organometallic chemistry as fields of study.[6] Emphasis was placed on elucidation

$$p\text{-}CH_3\text{-}(C_6H_4)\text{-}CH_3 \longrightarrow COOH\text{-}(C_6H_4)\text{-}COOH \qquad \text{Equation 1-1}$$

cat = $Co(OAc)_2$ in HOAc, Br^- promoter
200 °C
15 - 30 atm air

$$CH_2{=}CH_2 \longrightarrow CH_3CHO \qquad \text{Equation 1-2}$$

cat = $PdCl_2/CuCl_2$
100 °C
10 atm air

of reaction mechanisms and the discovery of new compounds that would catalyze transformations of organic compounds. Understanding the chemistry of these processes eventually would lead to improvements and enhancements of the catalysis. This understanding led to new growth in both fields, and formed the basis for new expansions of the chemistry and technology involved in catalytic oxidations.

The disciplines of homogeneous catalysis and organometallic chemistry are closely related. So much so, in fact, that a major justification for the study of organometallic complexes has been their potential use as catalysts. Even though the overwhelming majority of work in this area has dealt with mono-metallic systems, the field of multi-metallic catalysts is beginning to emerge as an area rich in potential for catalytic research. Systems containing more than one metal have several advantages over their mono-metal counterparts. Enhanced stability as well as synergistic interactions between the metals would give multi-metallic systems a range and versatility unknown in systems containing a single metal. In theory, the judicious choice of the combination of metals should

lead to a "tunable" catalyst system - one where selectivity or conversion is directly related to the metals involved.

The series of trinuclear metal carboxylate compounds is an ideal choice for carrying out such studies. Their versatility, combined with the wealth of knowledge available on the coordination chemistry of these complexes, make them excellent choices as subjects for the study of homogeneous catalysis.

Trinuclear Carboxylate Complexes

The family of trinuclear carboxylate complexes has been known in the chemical literature for over 100 years. Only in the more recent past have these complexes been extensively studied and characterized. These studies are extremely interesting in light of the versatility and uniqueness of multi-metallic systems in general. The synergistic effects of the presence of two or more metals in close proximity has been widely studied recently[7]; several varied applications of such systems are obvious in biochemistry and enzyme studies (tryptophan 2,3-dioxygenase, for example, consists of both a Cu(II) and an iron porphyrin in the active site)[8] as well as industrial processes involving transition metals on inorganic supports (SMSI interactions between Ti and Ru and other platinum metals in Fisher-Tropsch synthesis), and other commercial applications (oxidations by Co(II) involving Mn(II) as a cocatalyst, and the widely studied Ziegler-Natta polymerization system which involves the combination of Zr or Ti and Al as the catalytic species).

All of the trinuclear metal carboxylate complexes or "basic carboxylates"[9] discovered to date have virtually the same basic structure (Figure 1.2). (Although not trimers by the strictest definition, these trinuclear ruthenium carboxylates will be referred to as "trimers" for the sake of brevity.) The major differences in these systems occur in metal-metal distances and the planarity of the M_3-O core. The equilateral triangle formed by the metals (as the apices of the triangular M_3-O core) is bridged above and below the plane of the triangle by bidentate carboxylate ligands, and each metal is connected via a central, three-coordinate oxygen atom. Unlike their dimeric cousins,[7] these complexes contain no formal metal-metal bond. The remainder of the pseudo-octahedral configuration around each metal atom is completed by the ancillary ligand L. Obviously a great deal of versatility is inherent in these complexes - not only can the metals used be widely varied, but the carboxylate bridges and L also increase the permutations possible. To date, almost all of the first-row transition metals[10-14] have been isolated as "basic trinuclear carboxylates" (V,[15,16] Cr,[17-20] Mn,[21-24] Fe,[25-29] and Co[30-31]); others, like Ir,[32] Ru,[33-37] and Pd, Pt, and Rh[38-41] have also been prepared. Titanium[42] and zirconium[43] will also form a trinuclear complex slightly distorted from the traditional basic carboxylate structure involving a central hydroxy bridge between the metal centers. The carboxylate ligand can vary from acetate to butyrate for all of these compounds; partially chlorinated carboxylates as well as fluorinated ones have also been used. The ligand L is most often a classical coordination

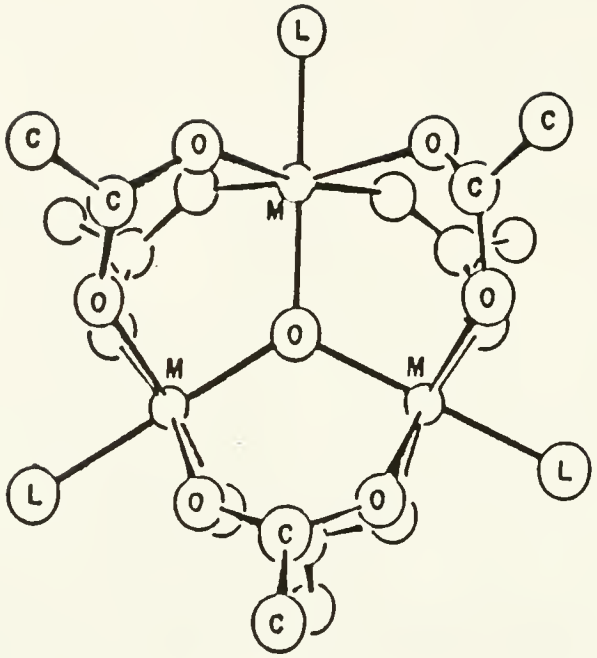


Figure 1.2 Generalized structure of basic trinuclear carboxylates having the formula $[M_3O(O_2CR)_6L_3]^n$.[44]

ligand such as pyridine, PPh_3, or even H_2O or diethyl ether. The last forms of variation take place in terms of the metals involved. As these complexes are most commonly isolated, the metals are found in the +3 oxidation state, causing the cluster as a whole to have a +1 charge. The other most commonly found form of these basic trinuclear carboxylates is one with one metal in the +2 oxidation state, rendering the complex neutral. In these systems, the assignment of oxidation states is truly a formalism. The iron and ruthenium complexes in particular can be classified as Robin and Day Class III compounds, indicating complete delocalization of the metal electrons. This classification is especially important in the trinuclear ruthenium carboxylates, the subject of this work.

This versatility has made this family of complexes choice candidates for a wide range of studies. The mixed-valence, neutral species (primarily the iron complexes) have been extensively studied in terms of intramolecular electron transfer reactions.[45-48] The manganese clusters, as well as similar dimeric systems, have been studied in hopes of elucidating the role of Mn in photosynthesis as well as for catalysis.[49-51] The more classical inorganic chemistry of these complexes has also been studied, including ligand-exchange reactions, for example.

Due to the vast information available on these trimers, it is not unreasonable to expect some studies in terms of their usefulness. The synergism expected to occur between the metal centers should manifest distinct differences from their monomeric analogs. The variety of oxidation states available, combined with

the ready exchange of ligands, makes these complexes ideal choices for catalysts, especially of homogeneous processes. Finally, the carboxylate ligands have been shown to be relatively inert to oxidation processes, as evidenced by the widespread use of metal acetates (specifically Co(II) and Mn(II)) and acetic acid in industrial oxidations.[52] For these reasons, the family of trinuclear metal carboxylate complexes would be expected to be good catalysts for a variety of homogeneous processes.

Only in the last few years have widespread attempts been made to utilize these complexes as catalysts. The cobalt acetate trimer ($Co_3O(OAc)_6(H_2O)_3^+$ and others) has been proposed to be one of the active catalytic species in the oxidation of p-xylene to terephthalic acid (the Mid-Century/Amoco Process).[53] It has also been shown to oxidize toluene and other hydrocarbons under relatively mild conditions.[13,30,31,53] Others have been used as catalysts as well. The rhodium acetate complex uses t-butyl hydroperoxide to selectively oxidize cyclohexene,[54] while the iron acetate trimers have been proposed to catalyze a variety of organic transformations.[55-57] By far the most widely studied (in catalytic terms) of these trinuclear species is the ruthenium complex.

More literature is available on the ruthenium system in both catalytic and chemical terms than most of the other trimers. These complexes were first isolated and characterized[33] in 1972; Spencer and Wilkinson found these trimers to be unique in the family of basic trinuclear acetates for several reasons. Both mixed-valence and cationic trimers were readily isolable. These complexes

underwent a one-electron non-reversible wave electrochemically, and readily underwent ligand exchange as well. The most unusual feature of the ruthenium trimers was the reversible removal of the central oxygen atom, a reaction unknown for the other trinuclear metal systems. Later studies by Meyer et al., expanded[58-62] the original electrochemical studies, revealing for the $Ru_3O(OAc)_6(pyz)_3$ (where pyz = pyrazine) complexes a series of five one-electron reversible waves. Four of these waves were attributed to the metal center, corresponding to formal oxidation state changes from Ru(III,III,II) to Ru(IV,IV,III). Linking these complexes into multinuclear oligomers revealed systems that would undergo up to ten one- or two-electron waves, justifiying the nickname "electron sponge" for these ruthenium complexes. A generalized MO scheme,[61] shown in Figure 1.3, shows several orbitals of the π system of the Ru_3O core in a relatively small energy range. For the cationic, Ru(III,III,III) complexes, all levels up to E_1'' are filled; the A_2' level is only partially occupied. The orbitals containing the metal electrons are virtually indistinguishable, the justification for the Class III label of delocalization. This depiction also helps explain Meyer's electrochemistry as well as other spectroscopic properties of these complexes.

In all likelihood, the electrochemistry revealed for these complexes prompted the widespread study of the ruthenium complexes as catalysts. Olefin hydrogenations were first studied[63] by Wilkinson; further studies were carried out both homogeneously and heterogeneously supported on a carboxylate resin by Rempel and

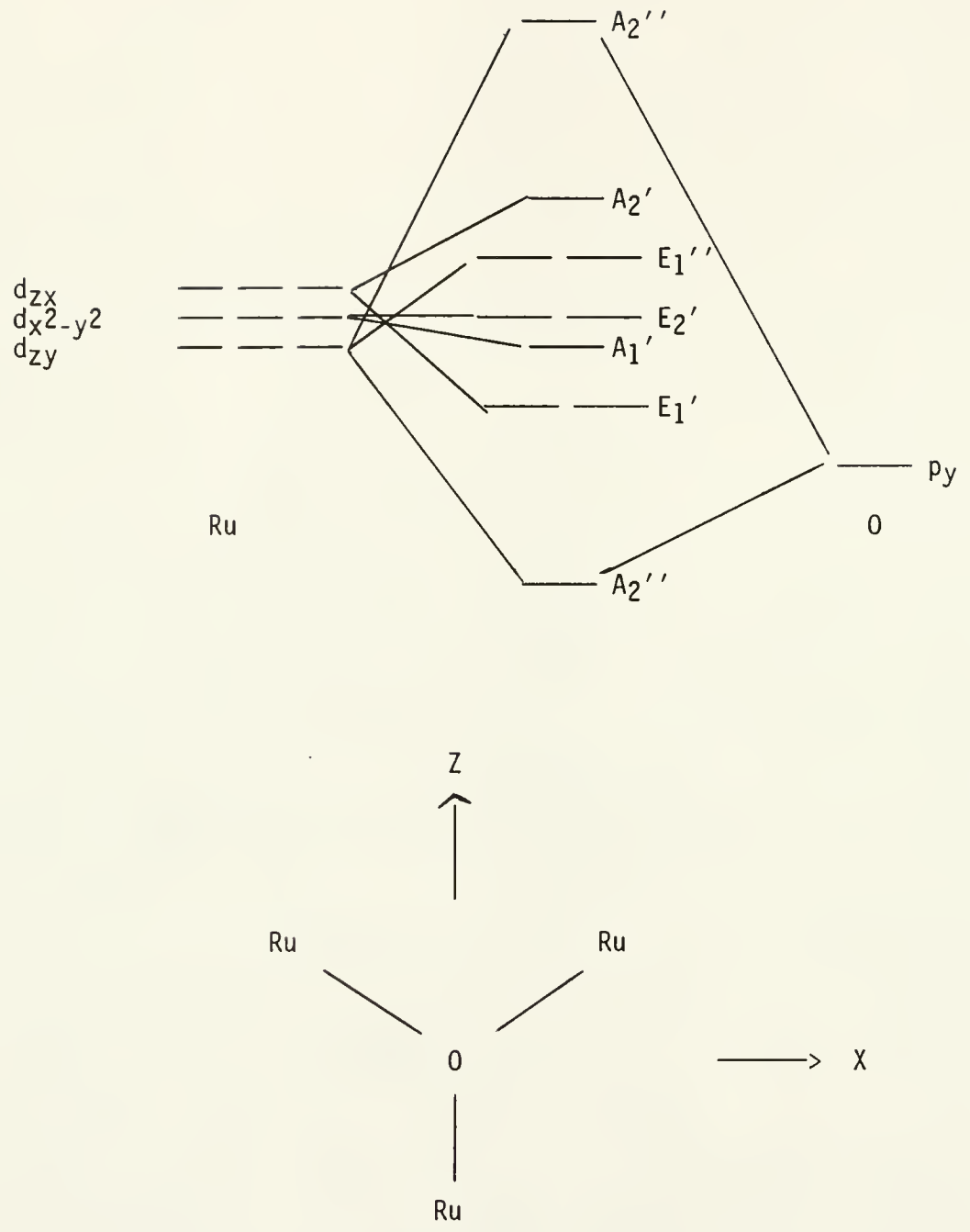


Figure 1.3 Qualitative molecular orbital description for $[Ru_3O(O_2CR)_6L_3]^n$ complexes, involving only the π system of the Ru_3O core. After Wilson et al.[61]

others.[64-66] Ziolkowski, et al,. have studied[13,67-69] the kinetics of cumene hydroperoxide decomposition and the exchange of DMF for H_2O using NMR techniques; they also have reported[13] some catalytic work in alkane oxidations. The ruthenium trimers have also been involved in the Prins reaction,[70] oxidative dehydrogenation of saturated carbinols,[71,72] and dimerization of acrylonitrile.[73] In terms of oxidation catalysis, the ruthenium trimers, in the presence of hydrogen peroxide, will oxidize substituted phenols to the corresponding hydroquinone.[74] In a mixed solvent system containing water, carbon tetrachloride, and acetonitrile, the Ru acetate trimer with periodate will oxidatively cleave alkenes,[75] similar to the traditional chemistry observed for RuO_4. They will also catalyze the isomerization of allylic alcohols.[76]

A study of the use of the ruthenium trimers as oxidation catalysts for a variety of organic transformations seemed potentially interesting, based on their previous use as catalysts and the large amount of electrochemical potential to be tapped in these complexes. The use of molecular oxygen as the primary oxidant has been an ongoing area of research, and the ruthenium trimers have not previously been shown to be active as catalysts in such a system. This work involved the continuation of the study of the oxidation of alcohols by the ruthenium carboxylate trimers,[44] as well as an extension of these catalytic studies to the oxidations of alkenes and alkanes by a new member of the trinuclear ruthenium carboxylate family, $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$, which has been synthesized and characterized.

CHAPTER II

ALCOHOL OXIDATIONS BY TRINUCLEAR RUTHENIUM CARBOXYLATE COMPLEXES

Introduction

The oxidation of alcohols is a procedure long known and used in organic chemistry for the production of aldehydes, ketones and carboxylic acids. Mild reagents, such as CrO_3/pyridine or MnO_2, react with alcohols to give primarily the carbonyl product (aldehyde or ketone). Stronger oxidants, like RuO_4, continue to oxidize primary alcohols through an aldehyde intermediate to carboxylic acids. Other high-valent ruthenium-oxo ions such as RuO_4^{2-} or RuO_4^- will oxidize primary alcohols to carboxylic acids, secondary alcohols to ketones, and will oxidize unsaturated alcohols without attacking the double bond.[77] Autoxidation of alcohols tends to produce ketone or acid along with hydrogen peroxide. Shell commercialized a process for the production of hydrogen peroxide by the autoxidation of 2-propanol (Eqn 2-1).[9]

$$(CH_3)_2C(H)OH \longrightarrow (CH_3)_2C{=}O + H_2O_2 \quad (98\%) \qquad \text{Equation 2-1}$$

The reaction of alcohols with noble metals such as Pd or Pt to give carbonyl products and a metal hydride species is well-

documented.[3,78] A mechanism involving a β-hydride elimination to give metal hydrides is generally assumed. This mechanism is also invoked for the Pd(II)-catalyzed oxidation of secondary alcohols to ketones with oxygen at 25 °C.[3]

A great deal of literature has been published on ruthenium-catalyzed oxidations of alcohols.[79] Besides the general uses of RuO_4, low-valent Ru(II) complexes have been widely studied as oxidation catalysts with both O_2 and milder oxidants such as iodosobenzene.[8] The most widely studied compound of this type, $RuCl_2(PPh_3)_3$, has been used to oxidatively dehydrogenate alcohols with oxygen.[80] With iodosobenzene, $RuCl_2(PPh_3)_3$ will selectively oxidize primary alcohols to aldehydes.[8] Sharpless et al. have found N-oxides combined with $RuCl_2(PPh_3)_3$ and other ruthenium compounds will also oxidize alcohols to their respective carbonyl products.[81] In benzene solvent, this complex preferentially oxidizes long-chain primary alcohols over the corresponding secondary alcohol.[82] Using O_2 as the primary oxidant, $RuCl_2(PPh_3)_3$ oxidizes allyl alcohols to α,β-unsaturated carbonyl complexes in a variety of relatively poorly coordinating solvents.[83] In all of these oxidations, several general trends arise. All of these oxidations are shut down in the presence of strong donor solvents like acetonitrile, indicating coordination of the substrate is necessary for oxidation to occur. Replacement of a coordinated nitrile by an alcohol is not highly likely. The mechanism consistently invoked for these reactions involves the coordination of alkoxides to a Ru(IV) species with subsequent β-hydride

elimination to give carbonyl product and a Ru(II) hydride. The hydridic species can be oxidized back to Ru(IV) by the available oxidant, creating a catalytic cycle.

A wide variety of other ruthenium compounds have also been used to catalyze the oxidation of alcohols. A ruthenium hydride, $RuH_2(PPh_3)_4$, catalyzes the condensation of alcohols to esters and lactones at elevated temperatures.[84] Monomeric ruthenium complexes containing fluorinated carboxylate ligands have also been shown to dehydrogenate primary and secondary alcohols via a β-hydride elimination pathway.[85,86] Slightly more active compounds containing diphosphine ligands have also been prepared and demonstrated to be catalytic.[87] The mixed-valence ruthenium carboxylate dimer $[Ru_2(OCR)_4Cl]$ has been shown to dehydrogenate methanol to formaldehyde under relatively mild conditions.[88] Ruthenium complexes as simple as commercially available ruthenium trichloride have also been shown to be active for both the oxidation of secondary alcohols and amines with oxygen.[89] Ruthenium(III) solutions will also oxidize allyl alcohol to acrolein.[90]

Ruthenium complexes containing large, bulky ligands have also been used for alcohol oxidations. Riley demonstrated a DMSO adduct of Ru(II), $RuX_2(DMSO)_3L$, would catalyze the aerobic oxidation of thioethers to sulfoxides. This reaction required a reducing solvent, alcohol, to reduce the Ru(IV) species back to the active Ru(II) complex, generating a carbonyl product.[91]

Bidentate imines have also been used with Ru(II) to oxidize coordinated alcohols in conjunction with O_2.[92] In these systems, a

Ru(IV) to Ru(II) cycle is again proposed as the pathway of the oxidation, and a disproportionation step enabling an escape from an inactive Ru(III) species to active Ru(II) and Ru(IV) complexes is also invoked. An unusual account of a Ru(III) complex containing 1,3-bis(2-pyridylimino)isoindoline (BPI) ligands is also involved in the oxidation of alcohols.[93] The use of Ru(III) is unusual in that Ru(III) complexes, generally low-spin t_{2g}^5, tend to be substitutionally inert.[94,95] Since the availability of open coordination spaces is a requirement for a feasible, selective homogeneous catalyst, Ru(III) complexes would not be expected to be vary active catalytically. Gagne's system was active for alcohol oxidations, producing around 60 turnovers (moles of product per moles of catalyst used) in 24 hours when a strong, noncoordinating base is present. Secondary alcohols formed ketones which were inert to further oxidation. Primary alcohols were oxidized initially to aldehydes (the primary product) which could react further giving acetals and other products. Again a disproportionation of Ru(III) to Ru(II) and Ru(IV) is proposed, with a Ru(IV)-coordinated alkoxide species as the active intermediate. Hydridic ruthenium(II) may be an intermediate in this reaction as well, arising from the β-hydride elimination of the Ru(IV)-alkoxide species.

T. J. Meyer has also contributed to this area with his well-studied ruthenium polypyridyl complexes. Extensive kinetic and mechanistic studies on alcohol oxidations by these high valent ruthenium-oxo complexes have been carried out.[96-98]

In light of the extensive, ongoing research into oxidations by ruthenium complexes in general, and the high potential for catalysis demonstrated by the trinuclear ruthenium carboxylate complexes, these particular complexes were chosen to screen as catalysts for the oxidation of alcohols by molecular oxygen.

Previous Work

Bilgrien discovered that $Ru_3O(prop)_6(H_2O)_3^+$ would catalyze the selective oxidation of primary and secondary alcohols to the corresponding carbonyl product using O_2 as the primary oxidant.[44] A wide number of alcohols were active in this system, and in all cases the only product formed was the aldehyde or ketone, with no traces of carboxylic acid observed. Several different trimeric ruthenium carboxylate complexes were found to be effective catalysts as well. These oxidations exhibit a slight rate dependence upon acidity, as demonstrated by the inhibition of the reaction upon the addition of acids. On the other hand, bases had a curious effect on the reaction. Sodium ethoxide enhanced the catalysis, 2,6-lutidine inhibited the reaction, and NaOH caused precipitation of the catalyst.

In mechanistic terms, Bilgrien found that for every mole of carbonyl product produced, a mole of water was formed as well, implying the four-electron reduction of oxygen to water.[44] Hydrogen peroxide, a likely intermediate in this process, was never detected in the reaction mixture. These complexes would also oxidize alcohols with H_2O_2 in place of O_2 as the primary oxidant. A rough calculation using the pressure drop of the pressure gauge for the O_2

consumption showed that for each mole of O_2 consumed, two moles of product are produced. The rate of the reaction in terms of oxygen pressure was found to be .25. The catalyst did not seem to decompose during the reaction, as indicated by both IR and ^1H NMR results. Bilgrien also found that the mixed-valence trimer was readily oxidized by O_2 in alcohol solution to the Ru(III,III,III) complex, but the reduction of this species by alcohol did not occur.

Bilgrien's mechanism for the ruthenium trimer-catalyzed oxidation of alcohols is shown in Figure 2.1.[44] This scheme invokes the Ru(III,III,II)-alcohol species as the active intermediate, which undergoes intramolecular disproportionation to form a Ru(IV,II,II) ruthenium species. The decomposition of this intermediate could occur via a number of pathways, the most likely of which involves a two-step reduction of the alcohol by the trimer. This reduction would generate the Ru(II,II,II) species, without the central μ_3-oxygen first observed by Spencer and Wilkinson,[33] which would readily be oxidized back to the Ru(III,III,II) intermediate in the presence of O_2.

Scope of Catalysis

Apparatus. All pressurized oxidations were carried out in slightly modified Parr hydrogenation setups (Figure 2.2). This apparatus has previously been described in detail by Zuzich and Bilgrien.[44,99] For these oxidations, stainless steel pressure heads, constructed from Swagelok fittings and equipped with standard sample valves, gas gauges, were also equipped with pressure relief valves as a safety precaution. This apparatus was directly

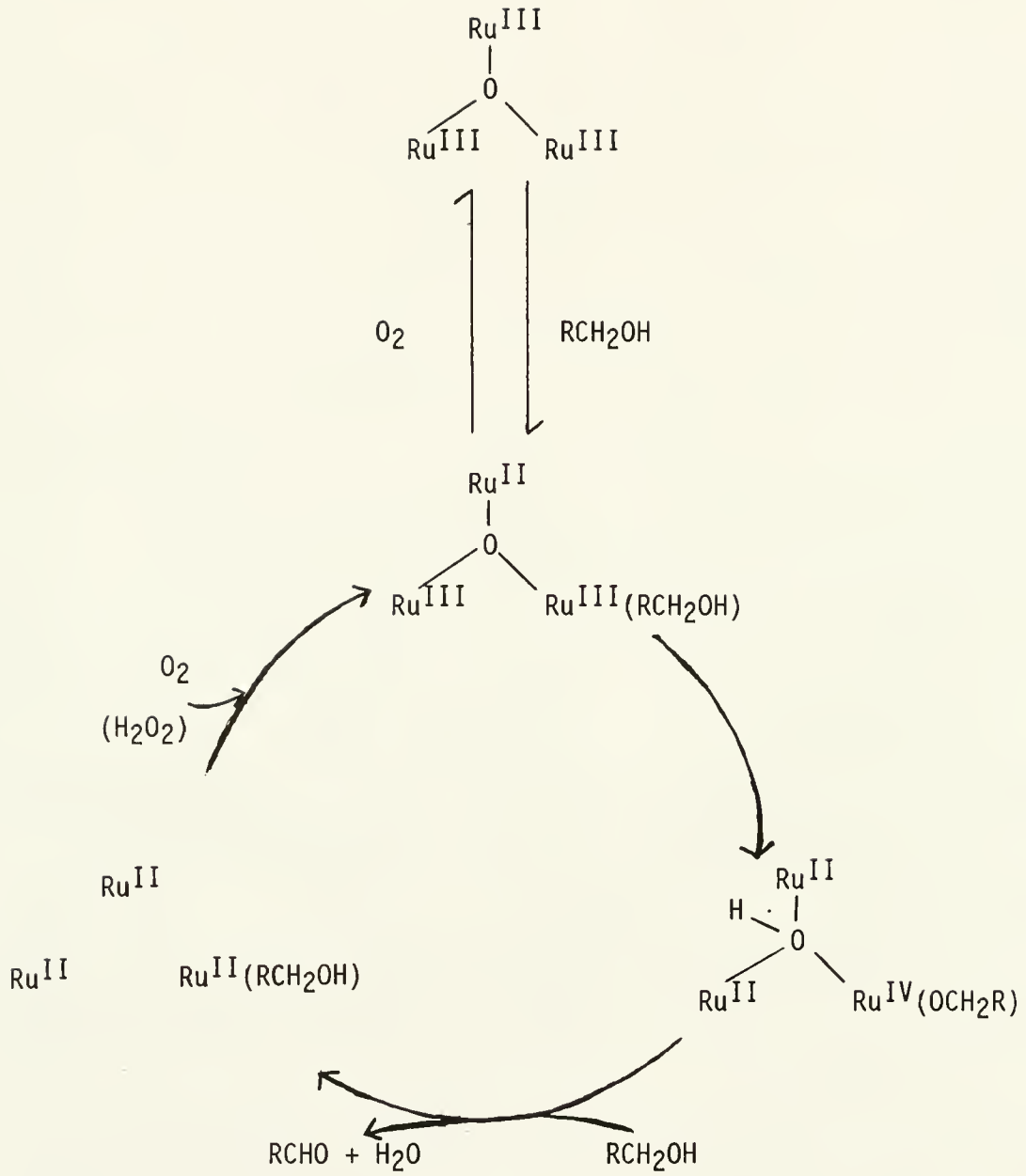


Figure 2.1 Bilgrien's proposed mechanism for the oxidative dehydrogenation of alcohols by $[Ru_3O(O_2CR)_6(L)_3]^n$. Other ligands have been omitted for clarity.[44]

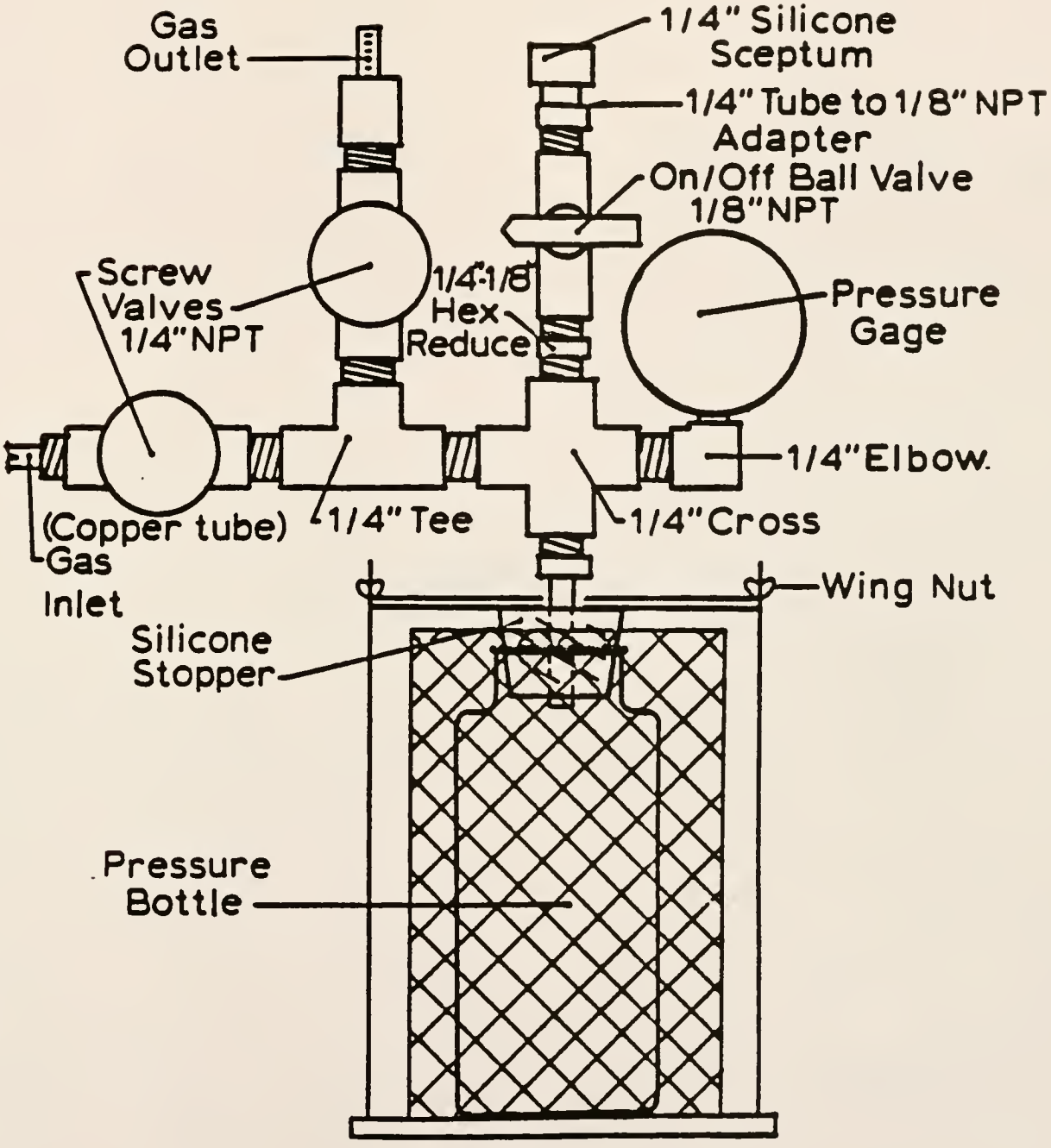


Figure 2.2 Schematic diagram of a standard pressure head without safety release valves.[99]

connected to an oxygen tank by copper tubing. The direction and path of exit gases were controlled by a length of tygon tubing attached to the exit valve which ran to the back of the hood. A glass, 250ml, Parr hydrogenation bottle (the reactor vessel) was attached to this apparatus by a #6 silicone gum rubber stopper and a metal cage. The bottle is surrounded inside of this cage by an aluminum sheath, designed to theoretically reduce the amount of glass shards that would be produced in an explosion.

Sampling techniques have been previously described in detail by Bilgrien.[44] Briefly, a 1-mL gastight stringe, equipped with a Leur-lok syringe valve and a 12-inch needle, is inserted through the septum at the top of the pressure head with the valve closed. The needle is guided through the ball valve into the reaction mixture. The syringe valve is opened, a small aliquot withdrawn (~.2 mL), the valve closed, and the needle withdrawn. With practice, this procedure can be accomplished quickly, safely, and with no observable pressure loss. The aliquots are analyzed using GC, GC/MS, and GC/IR.

Oxidation procedure. Typical oxidations involved 50 mL of alcohol (as both solvent and substrate), 1 mL ketone standard, and 10^{-5} moles of catalyst. Reactions were carried out in a 65 °C silicone oil bath monitored by an Omega 6100 temperature controller and thermocouple under initial pressures of 40 psig of O_2. Stirring rates of the solutions were controlled by magnetic stirrers beneath the oil bath; the oil bath was circulated by an overhead stirrer.

A slightly modified version of Bilgrien's technique[44] was used for the alcohol oxidations. The pressure bottle was charged with all components of the reaction except catalyst (i.e., substrate, standard, and a stirbar), covered with Parafilm, and placed in the oil bath to equilibrate for 20 - 30 minutes. The catalyst was added to the warm solution, the apparatus assembled and pressurized, placed in the oil bath, and a sample withdrawn. This sample was denoted as time zero and the start of the reaction. The reaction was stirred as rapidly as possible to ensure the saturation of the solution by O_2.

Safety precautions. CAUTION! Combinations of warm organic liquids and dioxygen are potentially explosive. Great care should be taken, especially during setup and dismantling of oxidation reactions, to avoid sparking the reaction mixture and causing a violent explosion. General safety precautions to follow include (1) let the reaction mixture cool to room temperature before depressurizing; (2) be sure outlet gases are directed away from any source of sparks; and (3) become aware of the explosion limits of solvent, substrates, and the oxidant (whether air or O_2) before beginning an oxidation.

Calculations. Amounts of products formed were determined by GC in all cases. Calibration curves relating moles of product to relative peak areas were constructed for all products formed. Standard procedure involved making up a series of solutions containing a varying, known amount of product, and a constant amount of standard in the solvent (alcohol) used. Repeated (at least five)

injections of each of these solutions gave a statistically valid value for the area percent of the product peak. Knowing the number of moles of product and standard in each solution gave a mole ratio of product to standard, which can be plotted against the ratio of the area percents of the product and standard. The area percents are obtained electronically from the integration of the peak areas of the GC chromatogram by an integrator. From the graph of mole ratio to area percent ratio, the number of moles of product can be obtained, if the amount of standard added is known.

Results and Discussion

Although Bilgrien's proposed mechanism adequately described the experimental data,[44] further work remained to be done to substantiate this proposal. Areas to be addressed included the differences in terms of activity between the mixed-valence and the cationic trimers, and the fate of the catalyst during the reaction. Other substrates should be tested, and more kinetic data should be accumulated as mechanistic support. For these reasons, this research project was continued.

Bilgrien found the activity of the ruthenium trimer catalysts varied greatly depending upon the amount of purification of the complex.[44] Liquid chromatography on a four-foot Sephadex LH-20 size-exclusion gel gave the best results, with dramatic effects on the catalysis, as shown in Figure 2.3. A general activity curve for the ruthenium propionate trimer, the standard catalyst for most of the remaining reactions, is shown in Figure 2.4.

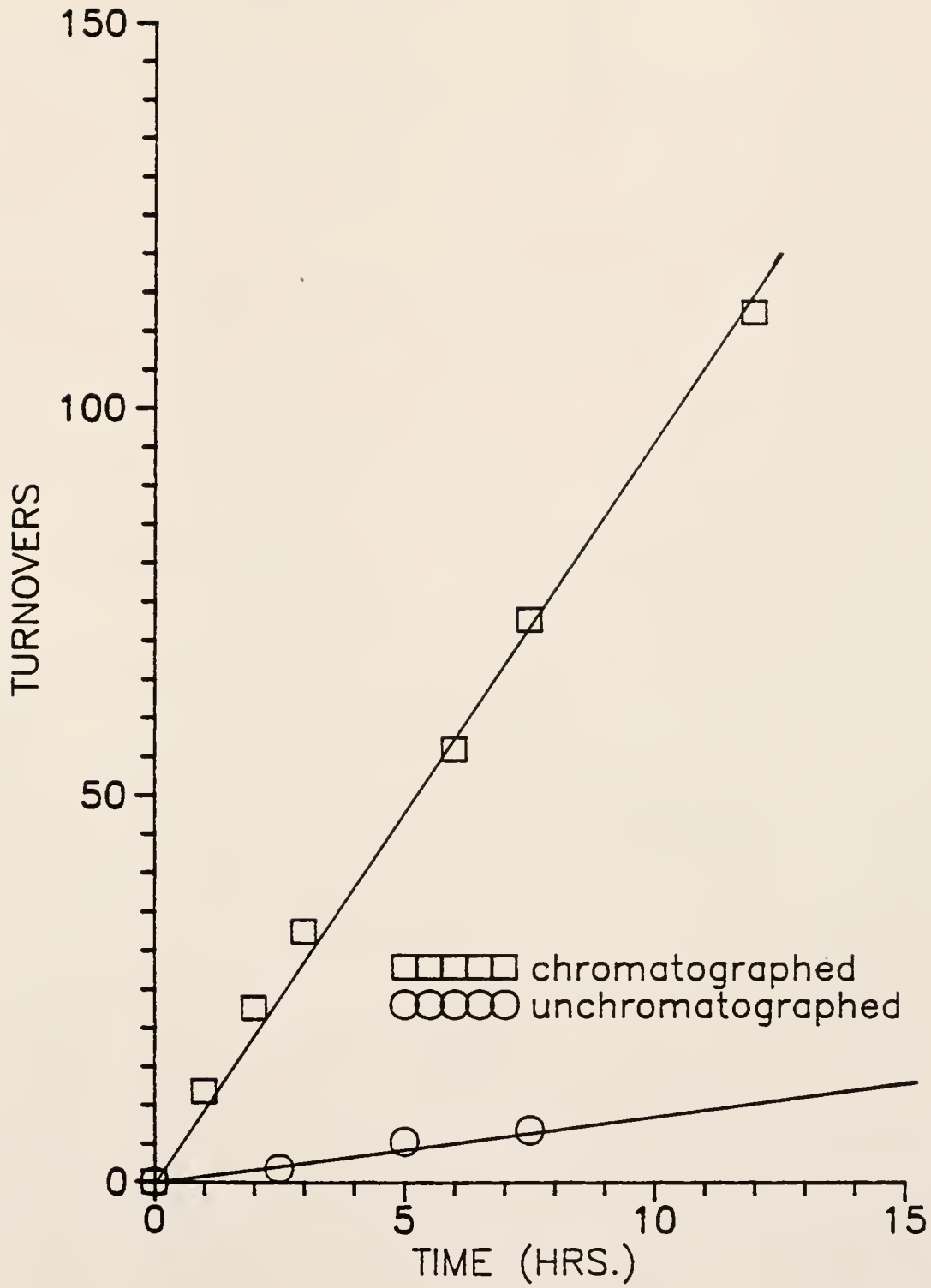


Figure 2.3 Chromatographed vs. unchromatographed $[Ru_3O(prop)_6(H_2O)_3](prop)$ in isopropanol oxidations.

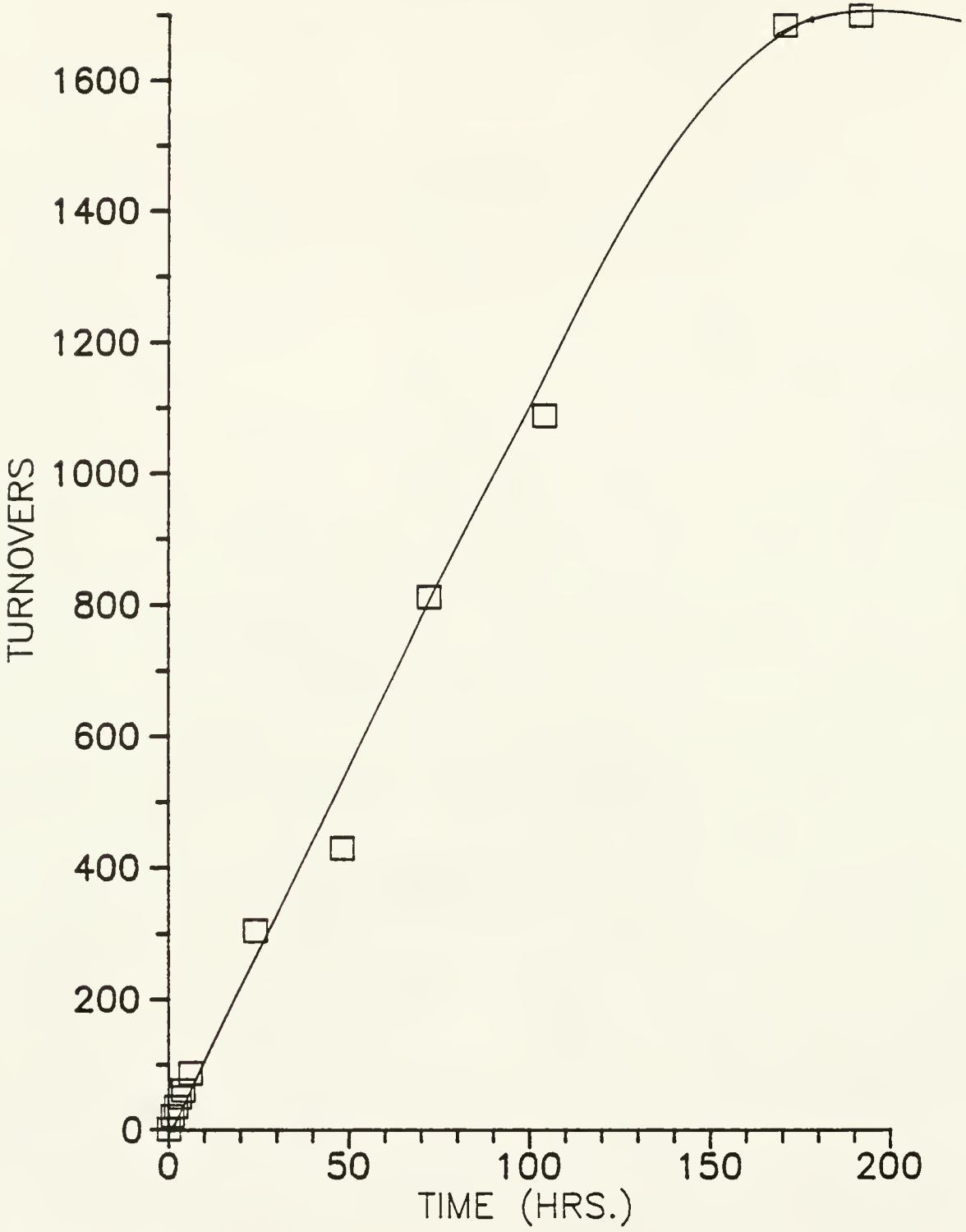


Figure 2.4 Activity curve for $[Ru_3O(prop)_6(H_2O)_3]^+$ - catalyzed isopropanol oxidations.

Other alcohol substrates were screened to further test the versatility of these trimers as catalysts (Table 2-1). Benzyl alcohol, as expected, produced only benzaldehyde, and allyl alcohol was exclusively oxidized to acrolein. Both of these substrates were oxidized significantly slower than the isopropanol oxidation used as the common standard for comparison in Bilgrien's work. While isopropanol oxidations resulted in 147 turnovers in 12 hours, these substrates only produced 40. Bilgrien also found the rate of reaction slowed as the substrate varied from primary to secondary alcohols. These substrates follow this general trend, as the rate of reaction for both benzyl and allyl alcohol is slower than that for either primary or secondary alcohols. This reduction in rate for benzyl alcohol is most probably due to steric bulk and subsequent hindrance in binding the substrate to the metal center. The oxidation of allyl alcohol is slower due to a different mode of substrate binding similar to that proposed by Taqui Khan.[90] In the $RuCl_3$-catalyzed oxidation of allyl alcohol by O_2, the substrate is bound in two sites around the octahedral ruthenium center - once by the double bond and once at the OH moiety. A β-hydride transfer creates a Ru(III) hydride-alcohol(+) species which is quickly oxidized by O_2 to give acrolein and the regenerated catalyst. No hydride species is postulated for the trimers, but the relative slowness of the reaction could be attributed to the inability of the alcohol to bind at the olefinic site (vide infra), and a loss of stability in the reduced ruthenium-alcohol intermediate.

Table 2-1

Alcohol Substrates[a]

substrate	T (°C)	product	to/12 hrs[b]	to/24 hrs[b]
ethanol[c]	25	No reaction	----	----
	65	acetaldehyde	198	313
isopropanol[c]	65	acetone	147	254
	100	acetone	685	1015
n-propanol[c]	65	propanal	430	645
n-butanol[c]	65	butanal	d	d
cyclohexanol[c]	65	cyclohexanone	d	d
t-butanol[c]	65	No reaction	----	----
benzyl alcohol	65	benzaldehyde	40	e
allyl alcohol	65	acrolein	42	e
50% isopropanol[f]	65	acetone	75	e
phenol[g]	65	No reaction	----	----

a) reaction conditions are as outlined under "Scope of Catalysis"

b) to = turnovers defined as moles of product/moles of catalyst used

c) from Bilgrien[44]

d) not quantified

e) reaction run for only 12 hours

f) auxiliary solvent used was acetonitrile as 50% by volume

g) solvent used was acetonitrile

Another congener of the ruthenium carboxylate trimer family, $[Ru_3O(prop)_6(py)_3](PF_6)$, was synthesized.. A bar graph comparing all of the different trimers used in shown in Figure 2.5. The pyridine adduct is completely unreactive in the oxidation of isopropanol, indicating that coordination of the substrate in place of the ancillary ligand L is necessary for catalysis to occur. When graphed in terms of turnovers, the differences in the cationic and the mixed-valence trimers becomes even more striking than Bilgrien reported. The mixed-valence compounds are greater than three times more active than their cationic counterparts. These differences are made more enigmatic by the known reaction chemistry of these complexes. The Ru(III,III,II) trimers are readily oxidized to the Ru(III,III,III) complexes by O_2.[33] However, the non-lability of Ru(III) centers towards substitution is well-documented[94,95]; the Ru(III,III,III) trimer would be expected to exchange H_2O (or L) for alcohol ligands very slowly. Assuming coordination of substrate is necessary for oxidation to occur, the Ru(III,III,III) system should oxidize alcohols more slowly than the more labile Ru(III,III,II) counterparts. The exchange of ligands in the Ru(III,III,II) trimer would be faster, so that even if the oxidation of the trimer from the Ru(III,III,II) to the Ru(III,III,III) did occur, a molecule of alcohol would already be present in the coordination sphere of the catalyst. This would explain some of the differences in the catalytic activity of these complexes.

A comparison of the ruthenium trimers with other complexes reported in the literature to oxidize alcohols would be informative

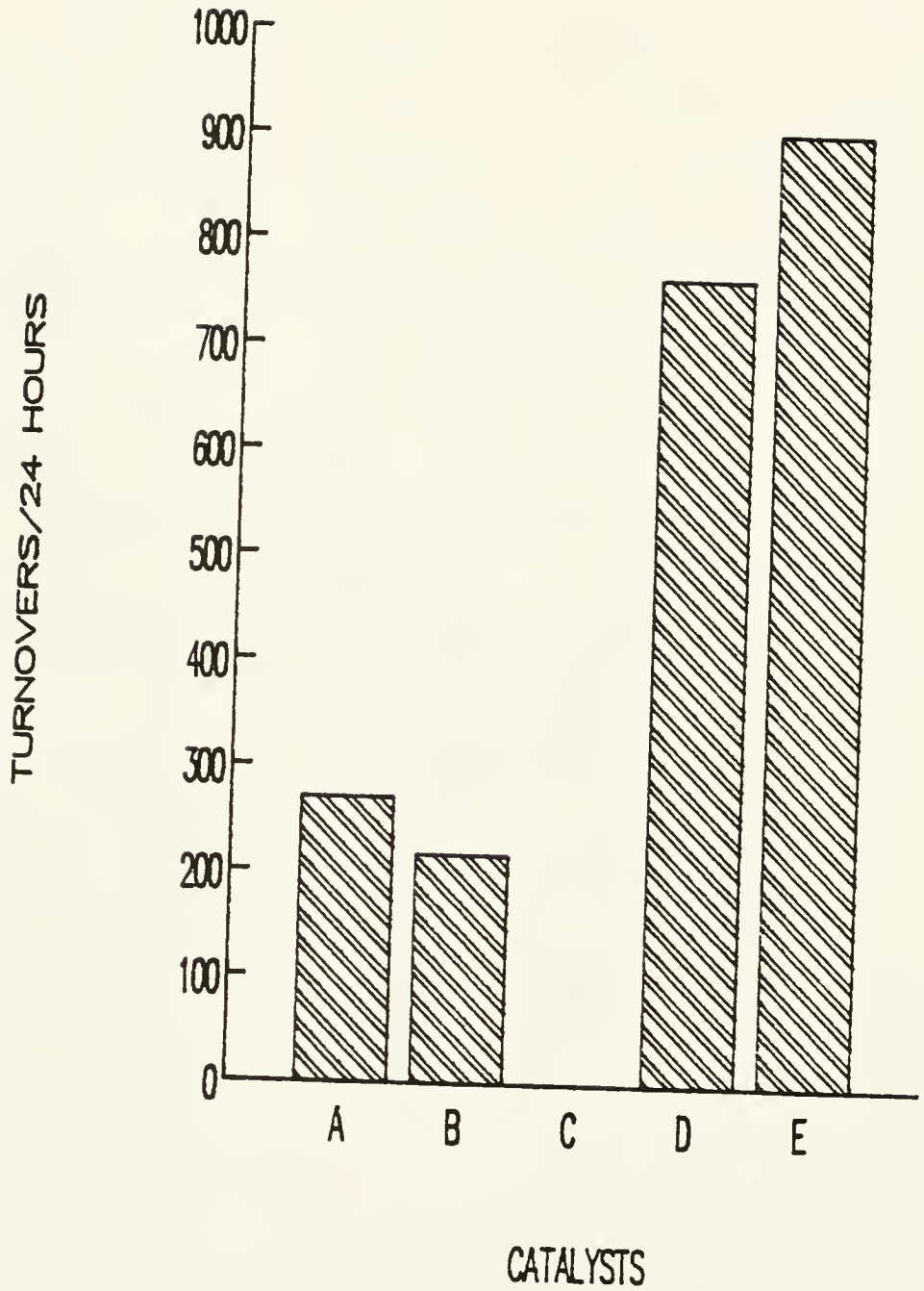


Figure 2.5 Comparison of $[Ru_3O(O_2CR)_6(L)_3]^n$ catalysts for isopropanol oxidations. (A) $[Ru_3O(OAc)_6(H_2O)_3]^+$ (B) $[Ru_3O(prop)_6(H_2O)_3]^+$ (C) $[Ru_3O(prop)_6(py)_3](PF_6)$ (D) $[Ru_3O(prop)_6(H_2O)_3]$ (E) $[Ru_3O(prop)_6(PPh_3)_3]$.

in terms of gauging the activity of this system. A graphical comparison is shown in Figure 2.6. As mentioned in the introduction to this chapter, both $RuCl_3$ and $RuCl_2(PPh_3)_3$ have been shown to oxidize alcohols using molecular oxygen as the primary oxidant.[80,89] Since the trimers also operate using oxygen, these systems should be enlightening for comparing relative reactivities of the catalysts. The trimers are approximately 10 times more active than the other ruthenium complexes attempted, on the basis of turnovers in 12 hours. Even taking into account that the trimers contain 3 moles of ruthenium per mole of catalyst, while the others only have one, the trimers are still over three times more active.

The mechanism of these oxidations could safely be assumed to not involve autoxidation pathways, due primarily to the selectivity observed in the reaction. If free radicals were involved in these oxidations, the further oxidation of aldehydes to carboxylic acids would be expected. However, acid products are not observed under our conditions, leading to the assumption the trimers are selective oxidants. To further justify this claim, typical reactions designed to prove or disprove free radical chain mechanisms were carried out (Figure 2.7). The addition of benzoquinone, a free radical trap, to a typical oxidation has no effect on the reaction. A free radical initiator, AIBN (azobis(iso-butyronitrile)), was added to the reaction in place of the catalyst and achieved approximately 10 turnovers in 1 hour and ceased to function. These experiments emphasize the non-radical nature of these oxidations.

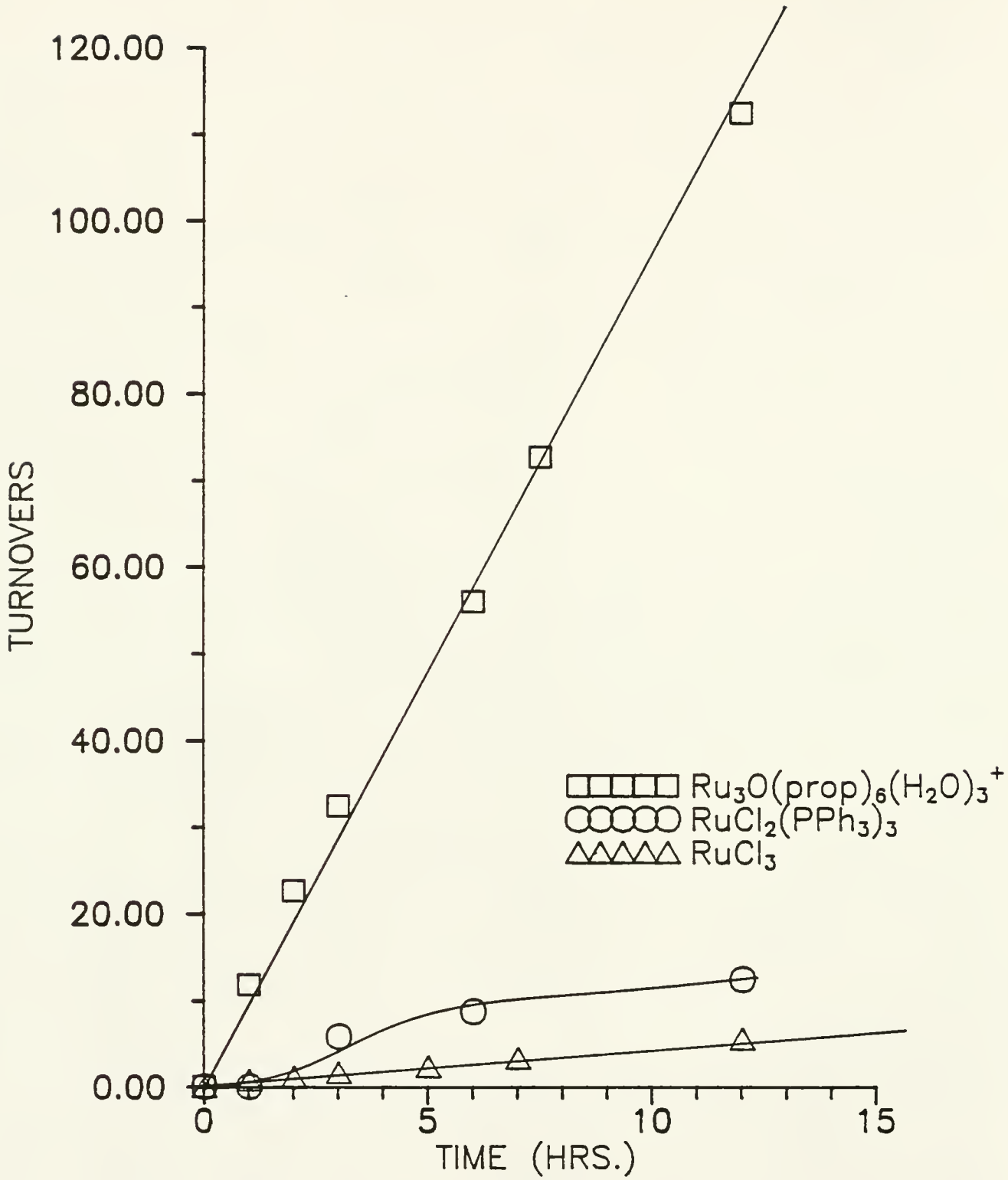


Figure 2.6 Comparison of various ruthenium catalysts in isopropanol oxidations.

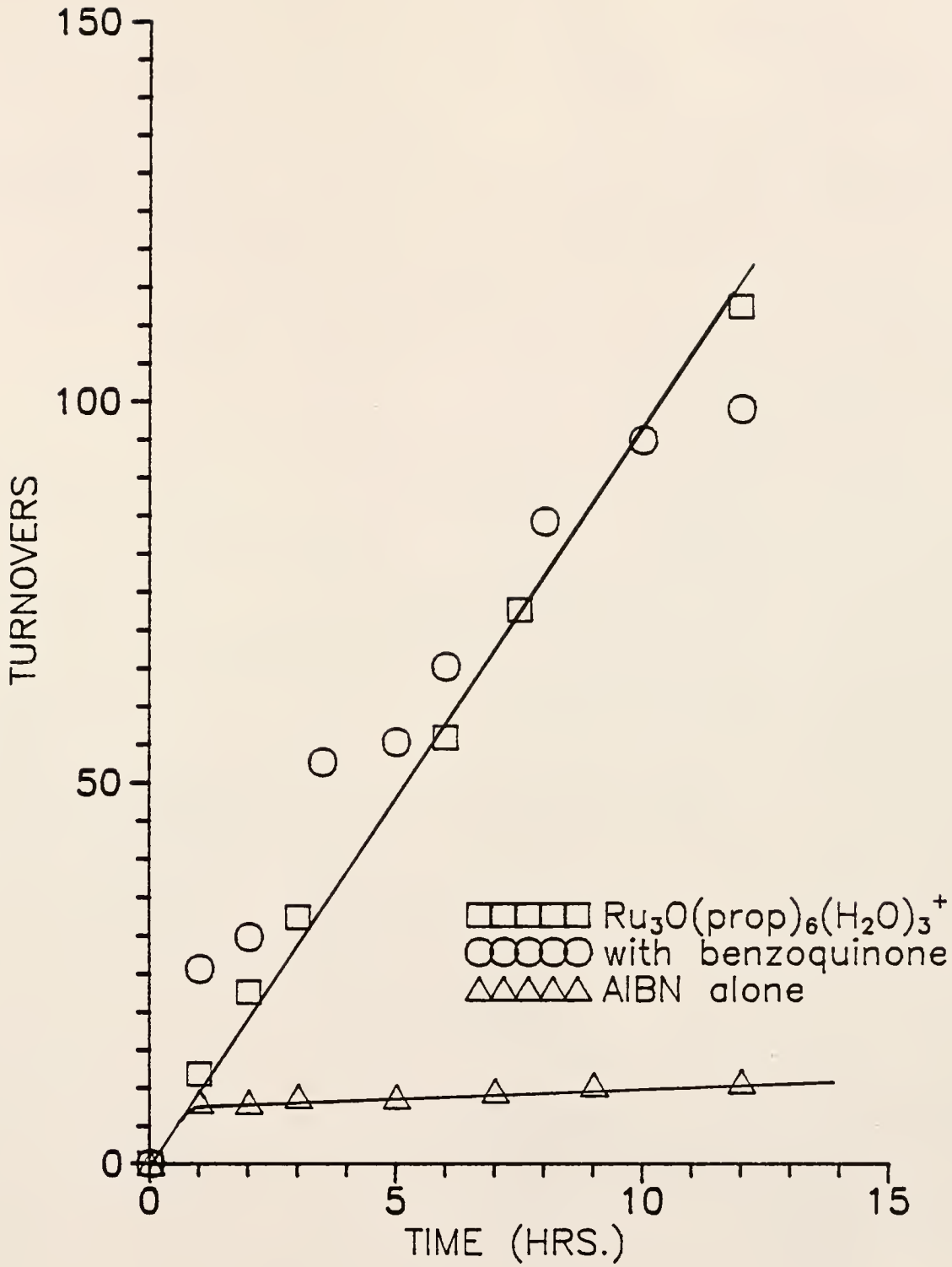


Figure 2.7 Free radical experiments in isopropanol oxidations.

Bilgrien noted that for every mole of product formed, one mole of water was also produced.[44] If the assumption the substrate must coordinate in order for oxidation to occur is valid, the effects of adding or removing water in the reaction should prove useful in determining a mechanism (Figure 2.8). The addition of 5A activated molecular sieves to the reaction greatly accelerated the rate, while a reaction run in a 50/50 mixture of isopropanol and water showed a drop in activity after about five hours. This curvature, indicative of catalyst deactivation, is not observed in the activity curve until after 180 hours of reaction time. Seemingly, the presence of water slowly inactivates the catalyst.

The catalyst does not seem to decompose during catalysis, according to ^{1}H NMR and IR.[44] UV-Visible spectroscopy has been very informative in determining the active species in solution. Since no induction period is observed for these oxidations, either the trinuclear carboxylate complexes is the active catalytic species, or it is a precursor that converts rapidly to the active species in solution. The lack of an induction period also indicates that the two different versions of the trimer (Ru(III,III,III) and Ru(III,III,II)) perhaps perform the oxidation by slightly different pathways. Bilgrien noted that while the Ru(III,III,II) could be oxidized to the Ru(III,III,III) in solution, alcohol was not a strong enough reducing agent to perform the reverse reaction.[44] However, a distinct color change is observed when an alcoholic solution of the catalyst is heated to 43 °C under an inert atmosphere. The changes were monitored via UV as shown in

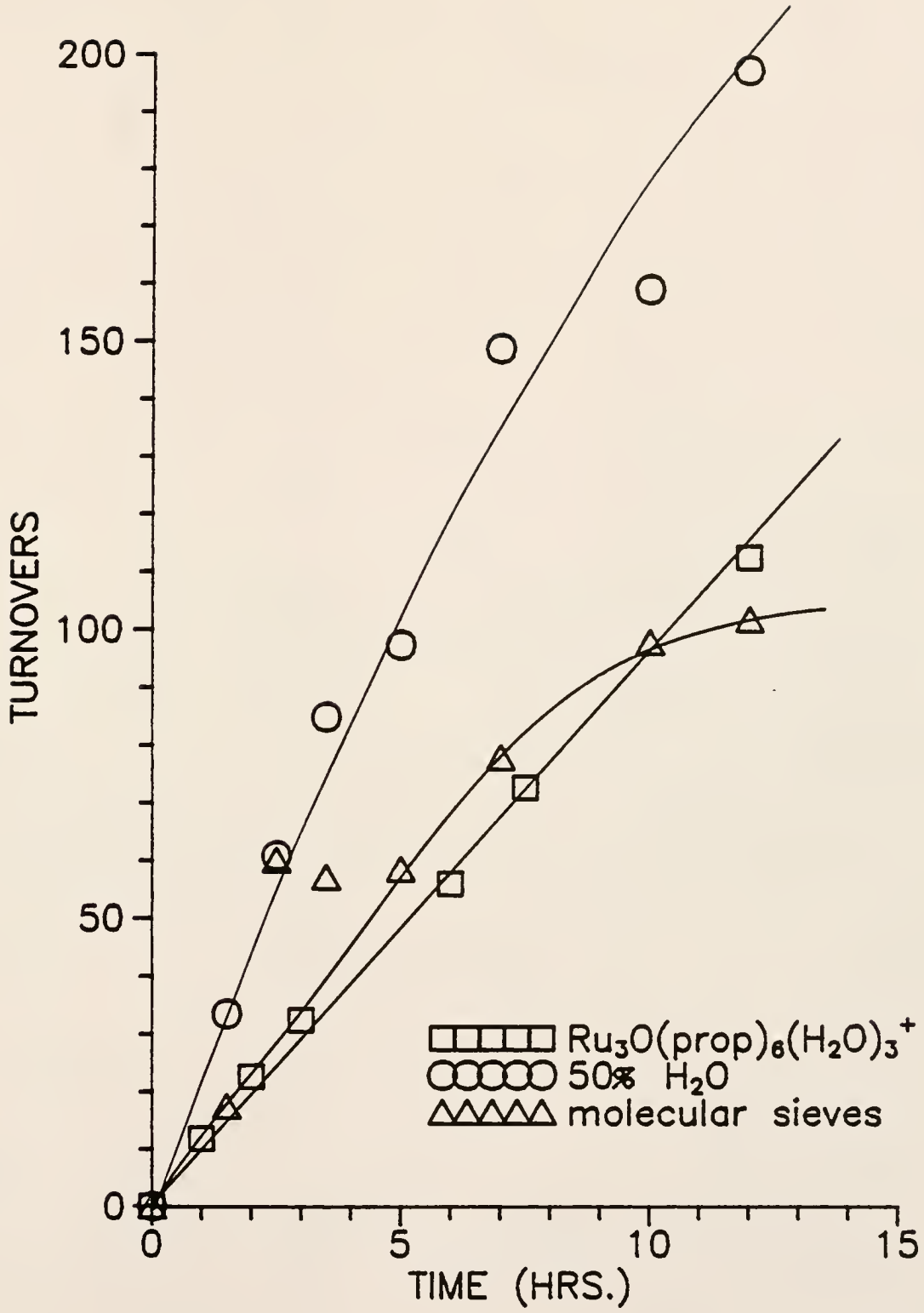


Figure 2.8 Effects of H_2O on isopropanol oxidations.

Figure 2.9. These changes correspond to the conversion of the Ru(III,III,III) to the Ru(III,III,II) complex as reported by Wilkinson.[33] To effect this change, the solution had to be heated for 18 hours. However, oxidations were performed at 65 °C, so this conversion may well occur under typical oxidation conditions. If this conversion were accompanied by production of ketone, the amount produced (assuming either a stoichiometric conversion either per mole of catalyst or per mole of ruthenium) was too small to be detected by GC. This change is reversible; the addition of O_2, 30% H_2O_2, or air to the warm alcohol solution immediately oxidizes the Ru(III,III,II) back to the Ru(III,III,III) with the corresponding color change. The color change corresponding to this conversion is not observed under our catalytic conditions; if present, the Ru(III,III,II) complex would be a transient species at best. These UV-visible studies indicate a Ru(III,III,II) intermediate created from a Ru(III,III,III) precursor would be a very slow but possible process. They give little or no information about the pathway used by a Ru(III,III,II) precursor, however.

The role of H_2O_2 in these oxidations was also pursued further. Figure 2.10 shows the effects of adding H_2O_2 to typical alcohol oxidations. Hydrogen peroxide is a potent oxidant by itself, as demonstrated by the upper curves. However, the ruthenium trimer catalyst will use peroxide in the absence of O_2 to oxidize alcohols to the same carbonyl products. If hydrogen peroxide is an intermediate in the reduction of O_2 as postulated by Bilgrien,[44] these graphs indicate the peroxide would be consumed as a co-oxidant

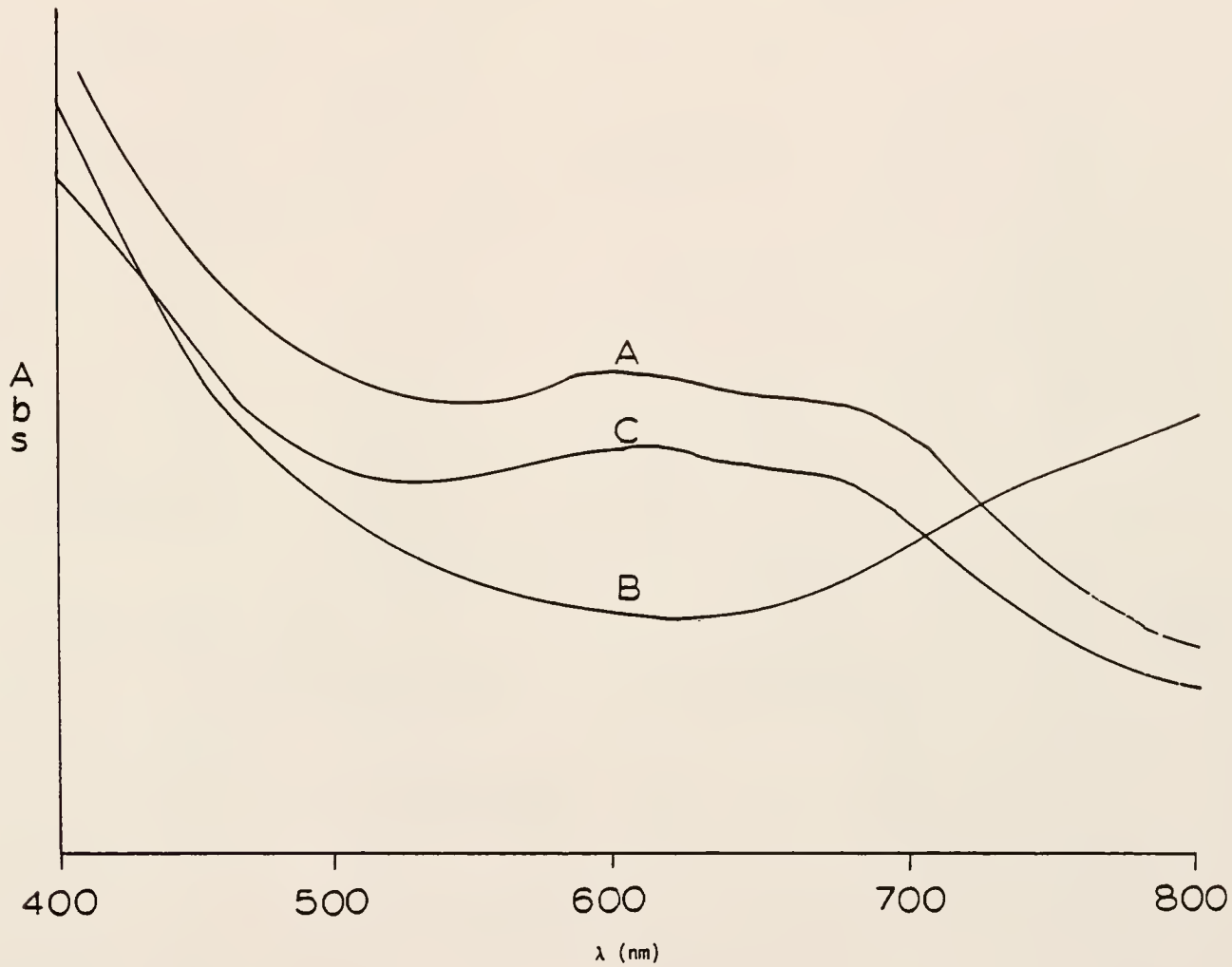


Figure 2.9 UV-Vis studies of $[Ru_3O(prop)_6(H_2O)_3](prop)$ (A)catalyst in ethanol under N_2, 25 °C (B) catalyst in ethanol under N_2, 43 °C (C) solution (B) exposed to O_2.

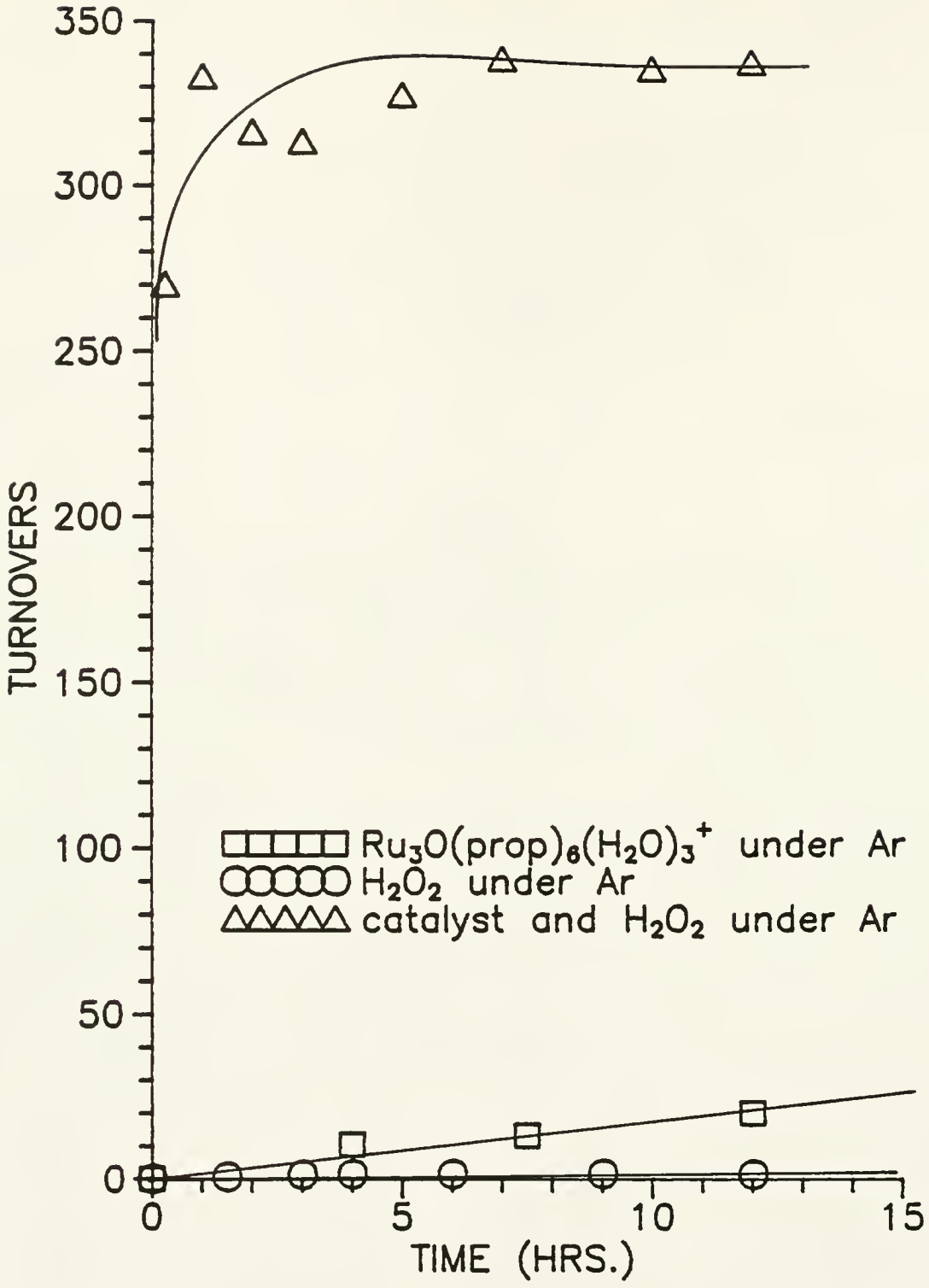


Figure 2.10 Role of H_2O_2 in isopropanol oxidations.

in the oxidation reactions. The amount of peroxide formed would, in all probability, be small and would be consumed as rapidly as it formed. A low steady-state concentration of peroxide would be one explanation for the failure to identify peroxide in the reaction mixture as well.

Determining kinetics in this system was based on the method of initial rates from initial concentrations.[100] The rate expression was assumed to take the form of Equation 2-2.

$$dx/dt = k_{obs}\,[cat]^a\,(PO_2)^b\,[substrate]^c \qquad \text{Equation 2-2}$$

In the alcohol oxidations, the substrate alcohol is present in much higher volume and the conversion of alcohol to product is relatively small. Therefore, the substrate concentration was assumed to be relatively constant, giving the rate equation 2-3.

$$dx/dt = k'_{obs}\,[cat]^a\,(PO_2)^b \qquad \text{Equation 2-3}$$

To obtain the order of the reaction with respect to each remaining component, one variable was held constant while the other varied. The rate of the reaction (dx/dt) was assumed to be the slope of the straight line obtained from a plot of mole of product formed vs. elapsed time. The appropriate mathematical manipulations gives a ratio of the rate laws which will yield a value for the reaction order.(Equations. 2-4,2-5,2-6).

$$(dx/dt)_1 = k'_{obs1}\,[cat]^{a}_{1}\,(PO_2)^{b}_{1} \qquad \text{Equation 2-4}$$

$$\frac{(dx/dt)_1}{(dx/dt)_2} = \frac{k'_{obs1}\,[cat]^{a}_{1}\,(PO_2)^{b}_{1}}{k'_{obs2}\,[cat]^{a}_{2}\,(PO_2)^{b}_{2}} \qquad \text{Equation 2-5}$$

Holding one variable constant (for example, (PO_2)) gives Eqn 2-6.

$$a = \frac{\log (dx/dt)_1 - \log (dx/dt)_2}{\log [cat]_1 - \log [cat]_2} \qquad \text{Equation 2-6}$$

Several reactions were run where each of the variables was changed in turn; this data is given in Table 2-2 and graphically in Figures 2.11 to 2.14.

Varying the concentration of the ruthenium catalyst (numbers 1, 4, and 5 in Table 2-2) lead to essentially first-order kinetics (Figures 2-11 and 2-12). Varying the oxygen pressure was slightly more demanding in that the total pressure had to be kept at 40 psig for comparison purposes (numbers 1, 2, and 3 in Table 2-2). The remainder of the pressure was made up of argon. The reaction order was found to be approximately .2 in O_2, very close to the value of .25 reported by Bilgrien (Figures 2.13 and 2.14).[44] For all practical purposes, however, the reaction could be considered zero-order in oxygen, considering the amounts of cumulative error in the analysis, calibration curves, calculations, and the differences in the values obtained mathematically and graphically.

A proposed mechanism for these oxidations is shown in Figure 2.15. This scheme differs significantly from that given by Bilgrien in several areas. The mechanism, beginning with the more labile

Table 2-2

Kinetic Data for Alcohol Oxidations
by $Ru_3O(prop)_6(H_2O)_3^+$

rate law = $dx/dt = k'_{obs}\,[Ru]^a\,(PO_2)^b$

Exp.	$[Ru]^a$ $[x\ 10^{-4}]$	PO_2 psig[b]	PO_2 n/v[c]	dx/dt^d x 10^{-3}	a[e]	b[f]
1	8.89	44.0	.108	8.60	1.10	.185
2	1.01	16.3	.040	7.16	----	.259
3	9.24	27.5	.0675	7.62	----	.119
4	2.80	45.5	.112	2.42	1.19	----
5	218.2	45.0	.110	22.3	1.33	----

a) Concentration calculated in moles/liter using 50 mL as the total volume.

b) Initial pressure of reaction in psig

c) N/v calculated from the ideal gas law (PV = nRT) assuming a volume of 270 mL and 65 ^oC.

d) dx/dt has units of molarity/hour; calculated as explained in text

e) $a = 1.20 \pm .12$

f) $b = .187 \pm .07$

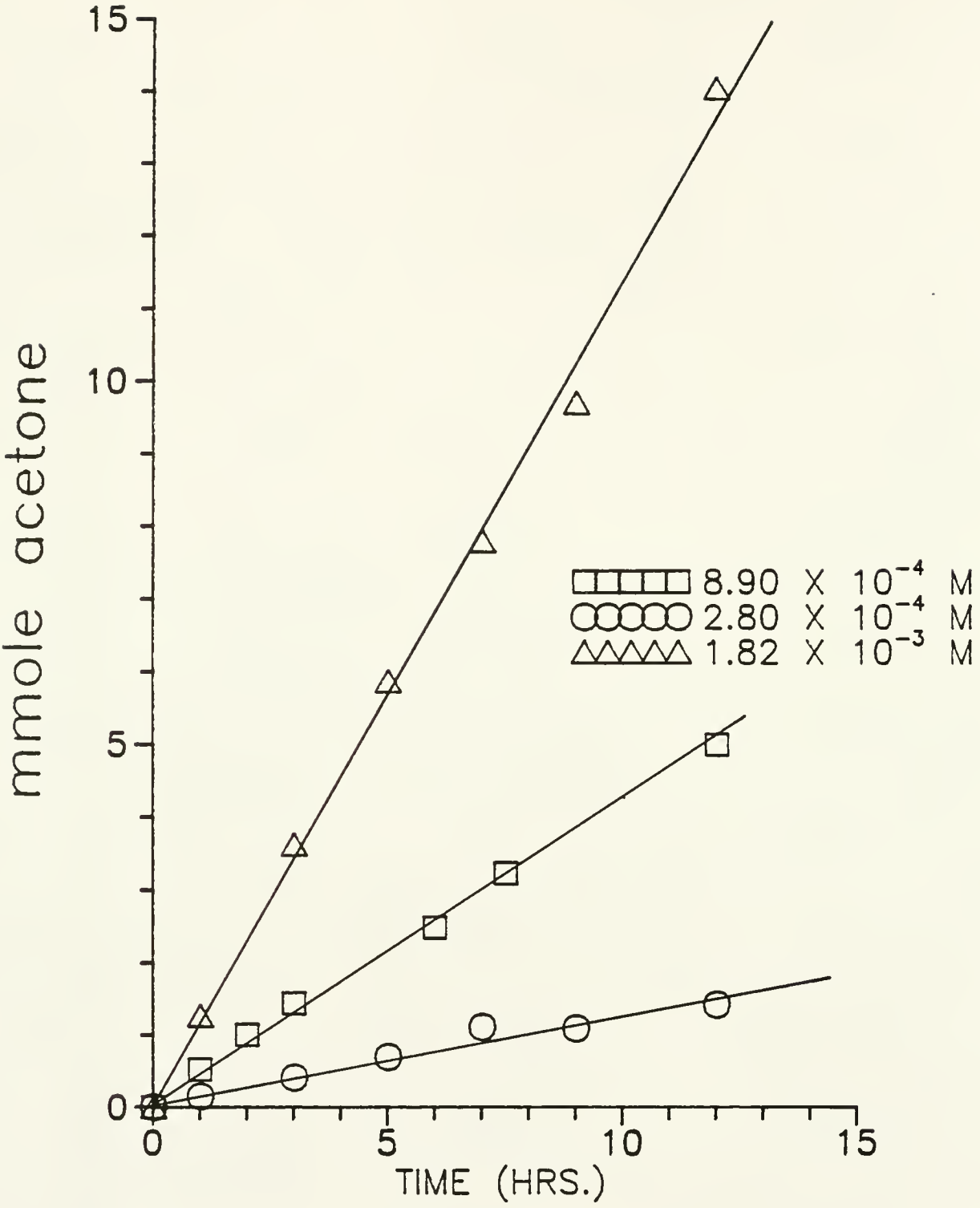


Figure 2.11 Kinetics: varying catalyst concentration.

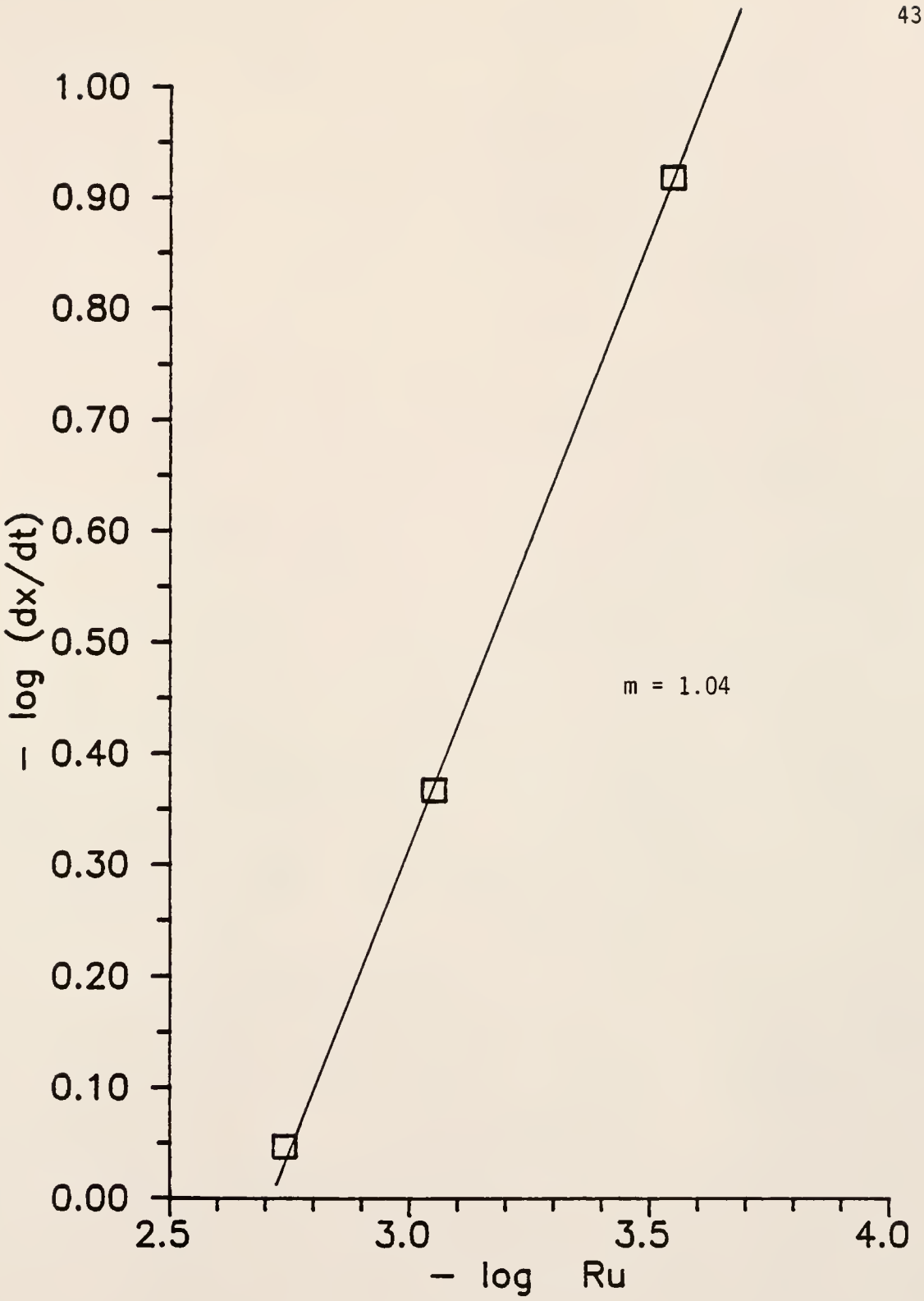


Figure 2.12 Kinetics: order in catalyst

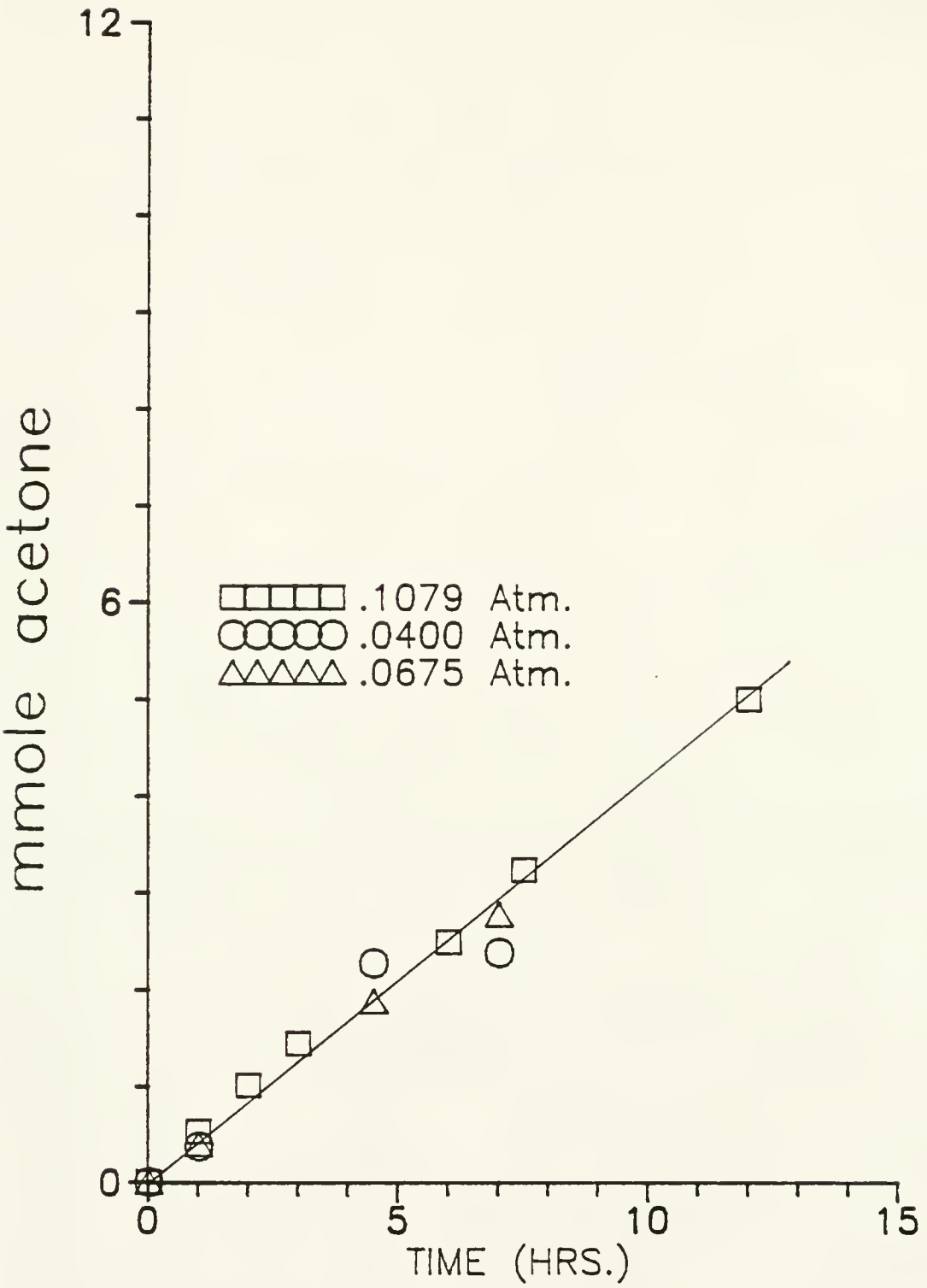


Figure 2.13 Kinetics: varying initial O_2 pressure.

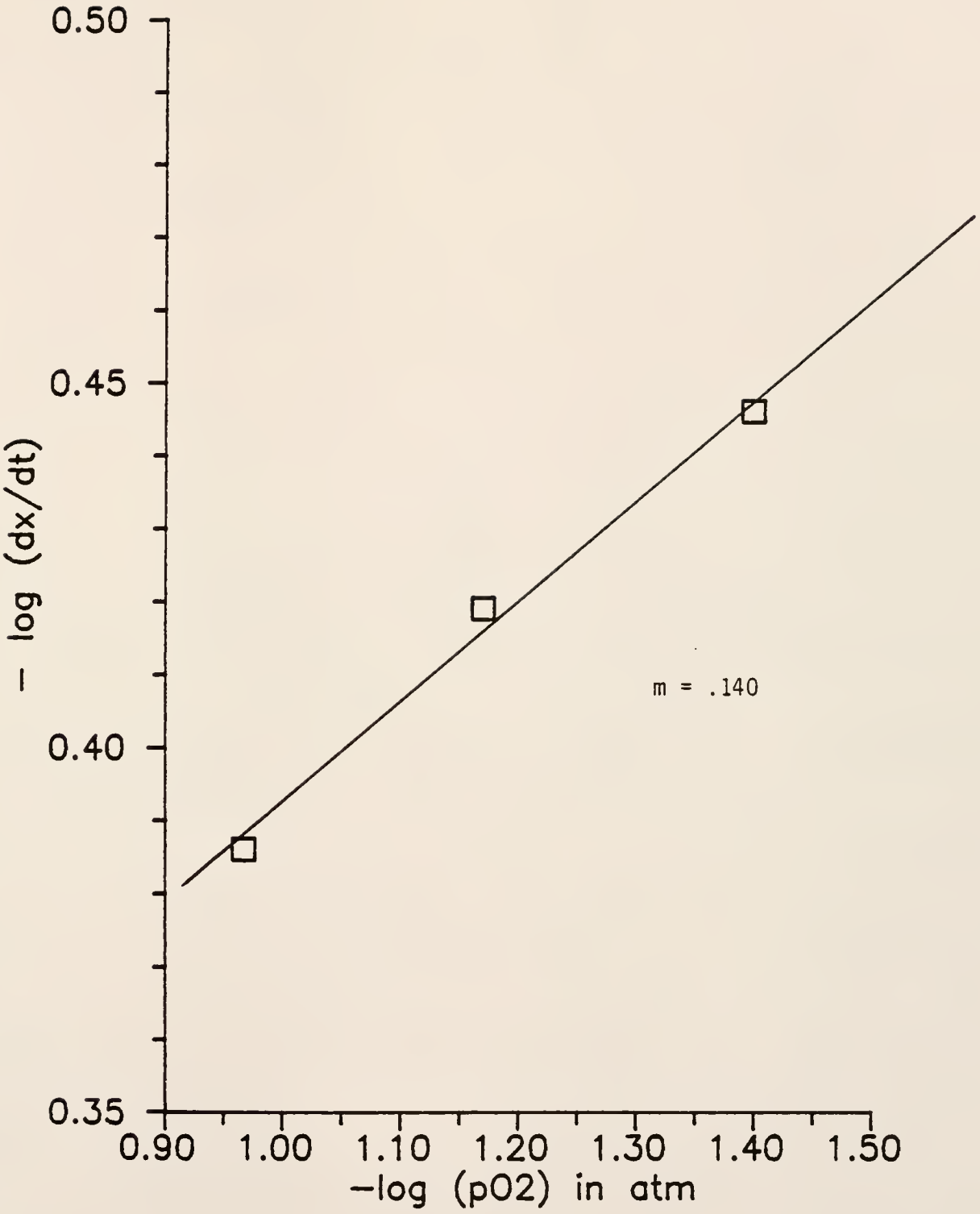


Figure 2.14 Kinetics: order in O_2.

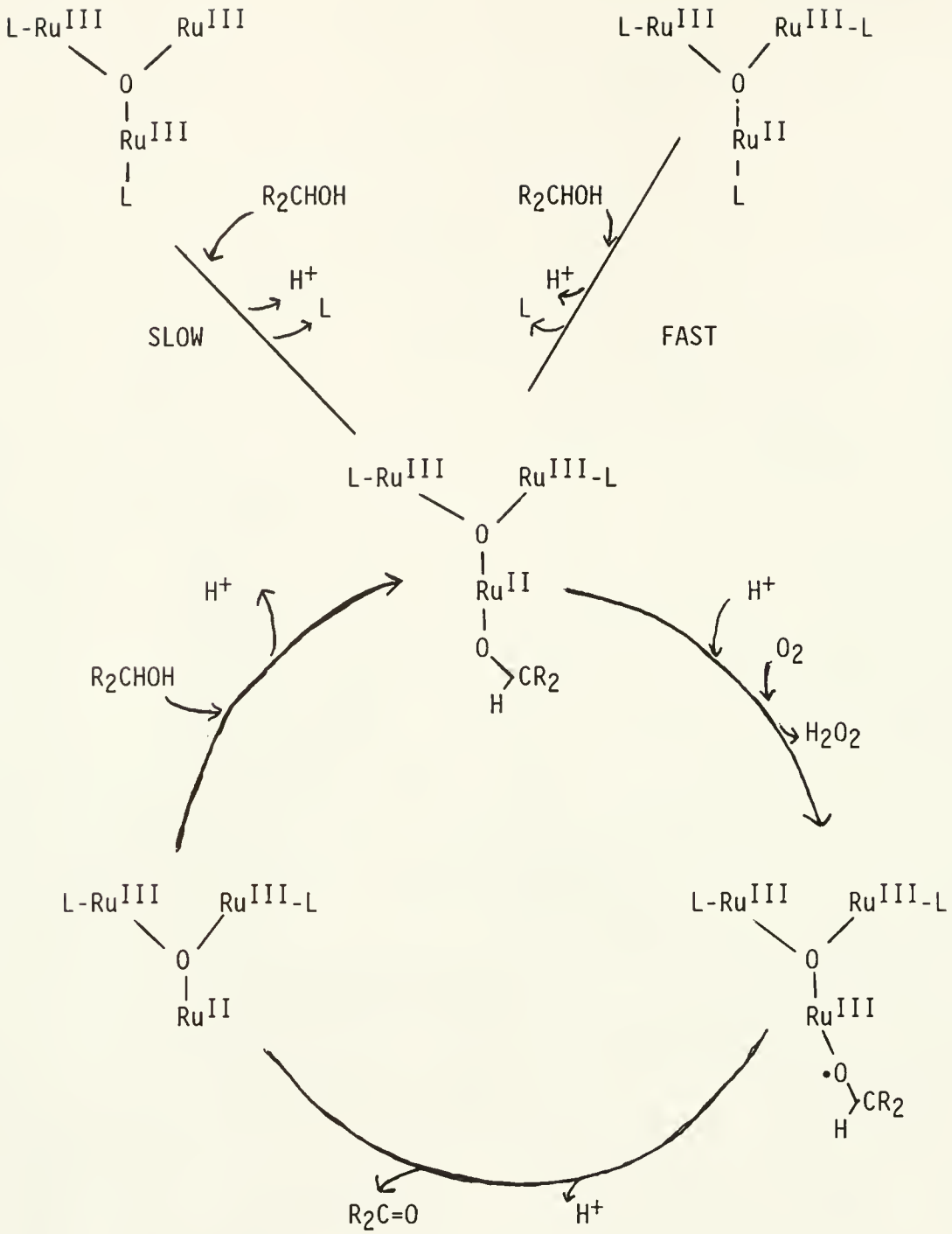


Figure 2.15 Proposed mechanism for the $[Ru_3O(O_2CR)_6(L)_3]^n$ - catalyzed alcohol oxidations. Carboxylate ligands have been omitted for clarity.

Ru(III,III,II) species, involves first replacement of the ligand L by a substrate molecule with concomitant loss of a proton. This Ru(III,III,II)-alcohol species is postulated to be the active intermediate in this cycle. Oxidation of this species by O_2 (or later in the cycle, H_2O_2) gives a species that can be formulated as a Ru(III,III,III)-alkoxy radical or a Ru(III,III,IV)-alkoxide species, depending on the placement of the extra electron. In Robin and Day Class III systems, this placement is more or less semantics. Reductive elimination from this species gives carbonyl product and a coordinatively unsaturated Ru(III,III,II) species. Solvation of this species by another mole of alcohol regenerates the active Ru(III,III,II) species.

The Ru(III,III,III) complex is slightly different in that to reach the active species it must undergo a one-electron reduction and replace L by a mole of alcohol. Ruthenium(III) species are, in general, substitutionally inert,[94,95] so the replacement step would be expected to be very slow. The UV-vis studies have demonstrated the reduction process to be slow as well. These two reasons help explain the differences between the two congeners.

The kinetics observed experimentally can be verified mathematically using the mechanism proposed in Figure 2.15. Each step in the mechanism can be written out and a rate expression derived for each step (Equations 2-7 through 2-17) using standard procedures and assuming the steady state approximation is valid for Equations 2-14, 15, and 16.

$$Ru^{3,3,2}\text{-}OH_2 + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{3,3,2}\text{-}OR + H_2O \qquad \text{Equation 2-7}$$
(A) (B) (H)

$$Ru^{3,3,2}\text{-}OR \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ru^{3,3,2}\text{-}OR + H^+ \qquad \text{Equation 2-8}$$
(B) (H) (C)

$$Ru^{3,3,2}\text{-}OR + O_2 \xrightarrow{k_3} Ru^{3,3,3}\text{-}\dot{O}R + O_2^{2-} \qquad \text{Equation 2-9}$$
(C) (D)

$$Ru^{3,3,3}\text{-}\dot{O}R \xrightarrow{k_4} Ru^{3,3,2} + R_2C{=}O \qquad \text{Equation 2-10}$$
(D) (E) (P)

$$Ru^{3,3,2} + ROH \xrightarrow{k_5} Ru^{3,3,2}\text{-}OR \qquad \text{Equation 2-11}$$
(E) (B) (H)

$$dP/dt = k_4(D) \qquad \text{Equation 2-12}$$

$$dA/dt = -k_1(A) + k_{-1}(B) \qquad \text{Equation 2-13}$$

$$dB/dt = -k_2(B) + k_{-2}(C) - k_{-1}(B) + k_1(A) = 0 \qquad \text{Equation 2-14}$$
$$k_{-2}(C) + k_1(A) = k_2(B) + k_{-1}(B) \qquad \text{Equation 2-14a}$$
$$k_2(B) = k_{-2}(C) + k_1(A) - k_{-1}(B) \qquad \text{Equation 2-14b}$$

$$dC/dt = -k_3(C)(O_2) + k_2(B) - k_{-2}(C) = 0 \qquad \text{Equation 2-15}$$
$$k_3(C)(O_2) = k_2(B) - k_{-2}(C) \qquad \text{Equation 2-15a}$$

$$dD/dt = k_3(C)(O_2) - k_4(D) = 0 \qquad \text{Equation 2-16}$$
$$k_3(C)(O_2) = k_4(D) \qquad \text{Equation 2-16a}$$

Rearrangement and subsequent substitution of Equations 2-14, 15, and 16 into the expression for dP/dt as shown below give the rate expression for dP/dt in Equation 2-20. This expression can be reduced to pseudo first-order in catalyst if $k_{-1}(B)$ is assumed to be

small. Under our conditions, a large excess of alcohol, the reverse reaction in Equation 2-7 should only occur to a small extent by Le Chatelier's Principle, so the assumption seems to be valid.

$$dP/dt = k_4(D) \qquad \text{Equation 2-12}$$
$$= k_3(C)(O_2) \quad \text{(from 2-16a)} \qquad \text{Equation 2-17}$$
$$= k_2(B) - k_{-2}(C) \quad \text{(from 2-15a)} \qquad \text{Equation 2-18}$$
$$= [k_{-2}(C) + k_1(A) - k_{-1}(B)] - k_{-2}(C) \quad \text{(from 2-14b)} \qquad \text{Equation 2-19}$$
$$= k_1(A) - k_{-1}(B) \qquad \text{Equation 2-20}$$

Equation 2-21 is the rate expression for the oxygen dependence obtained from the proposed mechanism. Through appropriate substitution from Equation 2-16a, this expression takes the form of Equation 2-22. This equation can be reduced to pseudo zero-order in oxygen pressure by assuming the concentration of D is constant throughout the reaction by the steady state approximation.

$$-dO_2/dt = k_3(C)(O_2) \qquad \text{Equation 2-21}$$
$$= k_4(D) \quad \text{(from 2-16a)} \qquad \text{Equation 2-22}$$
$$= k_4' \qquad \text{Equation 2-23}$$

This mechanism also accounts for the product/O_2 and product/water ratios previously observed by Bilgrien. An entire reaction, consisting of two complete cycles, will produce two moles of product while reducing one mole of O_2 to two moles of water. Hydrogen peroxide is most probably an intermediate in this reduction, although never positively identified because it is consumed as rapidly as it is formed.

A major driving force in this reaction is the large excess of alcohol available. Ordinarily, the replacement of ligands such as H_2O or PPh_3 by the poorly coordinating alcohol would be highly unlikely. However, with the large excess of alcohol available, the substitution occurs to a small extent. The low conversion rates observed in this oxidation (about 2%) are also explained by the small amount of substitution occurring in these systems. Interestingly enough, exchange of deuterated methanol for water in a mixed-metal (Ru_2Rh) acetate trimer has been observed in ^1H NMR.[101] Few detailed NMR studies of these complexes have been reported,[13,66,68] so this exchange may be more extensive than previously expected. The complete failure of the pyridine adduct to catalyze the oxidation, even after 24 hours, lends support to the idea of slow substitution by the alcohol substrate.

None of these theories, however, explain the surprising activity of the PPh_3 adduct. Of all the trimers screened as catalysts, the mixed-valence $Ru_3O(O_2CCH_2CH_3)_6(PPh_3)_3$ complex demonstrated the highest activity. Triphenylphosphine is expected to be a reasonably strong donor ligand toward Ru(II) (more than H_2O), so the substitution by alcohol should be significantly slower than for the aquo adducts. However, triphenylphosphine is very easily oxidized to the oxide, a very poor ligand. If all three phosphine ligands are removed and subsequently oxidized to triphenylphosphine oxide, the trimer would be essentially naked, and alcohol coordination would occur rapidly. The presence of triphenylphosphine oxide was never observed in the reaction mixture;

however, if this hypothesis is true, the quantities of the oxide would be minute (10^{-4} to 10^{-5} moles) and difficult to detect.

The question of nuclearity of the catalyst has yet to be addressed. The phosphine oxide hypothesis leads to the question of the number of ruthenium atoms active in the oxidation. In the case of the triphenylphosphine adduct, theoretically all three atoms could be involved in the oxidation. A mechanism similar to the proposal outlined in this chapter could be operating for each metal center, by virtue of the extensive delocalization over the Ru_3-O core. The synergism and interactions between the metals could support such reactions, as evidenced by Meyer's oligomers.[61] The spectral data show the catalyst is essentially the same before and after catalysis, and literature evidence is also available to support the assumption that the complex remains intact. Considering the volume of literature available on these complexes with no reports of decomposition during reaction, it is reasonable to assume that even under these stringent conditions the cluster retains its nuclearity. The only physical evidence available is the differences observed in the catalytic activity of the trimer compared to monomeric ruthenium systems. The large difference indicates the chemistry is somehow affected by three metals in close proximity, as was expected from the outset.

The series of trinuclear ruthenium complexes has not failed in its promise of producing highly intriguing chemistry. These complexes have been shown to catalyze the selective oxidation of alcohol to aldehydes and ketones by dioxygen. These oxidations are

presumed to occur via a standard Ru(II)-Ru(IV) cycle, but the cycle involves the reductive elimination of a Ru(III)-alkoxy radical. Based on these reactions, these complexes have upheld the potential promised by their electrochemistry. The unique role of three metal centers, intimately involved in a chemical transformation, has been demonstrated, and these complexes manifest unusual catalytic properties compared to monomeric species. Another enigma is their catalytic activity, considering that Ru(III) centers are traditionally inactive species in oxidations. The interactions between the metals in the trimers can also be supposed to overcome this trend, and in all probability, actually enhance the catalytic activity of this system. However, the versatility of these trimers has not been extensively tested.

Bilgrien found initially these complexes would not oxidize olefins in alcohol solvent.[44] However, changing the solvent to acetonitrile, widely used in oxidation studies for its inertness, drastically changed the chemistry. Under 40 psig of O_2, cyclohexene was oxidized to numerous products in the 12 hours. The volume of products formed generally is indicative of free radical chemistry, which is antipodally related to selectivity (vide infra). The oxidation of a substrate inert to free radical process, norbornene, was a complete failure. The lack of success in this area led to branching out into other trimers containing different ligands.

Experimental

Reagents and equipment. All reagents used were reagent grade or better and were, for the most part, readily available from

Aldrich Chemical Company. All alcohols were passed through a column of neutral alumina, purity checked by GC, and stored over activated molecular sieves. If necessary, the substrates were further purified by standard techniques. Prior to use, the alcohols were again passed through an alumina column.

GC analysis was performed on a Varian 3300 instrument utilizing packed, 8-ft, stainless steel columns and both FID and TCD detectors. Analyses and calibration curves were obtained using 15% DEGS (diethylene glycol succinate) on Chromosorb W (80/100 mesh). A Varian 4290 integrator automatically calculated peak areas and retention times. GCMS was performed on a service basis by Dr. R. W. King at the University of Florida. All IR spectra were recorded either as Nujol mulls or KBr pellets on a Nicolet 5DXB spectrometer and were background corrected. A Perkin-Elmer model 330 UV-visible spectrometer equipped with a circulating thermal bath was used to collect UV-vis spectra; all spectra were background corrected. Elemental analyses were performed on a service basis by the microanalytical laboratory at the University of Florida.

Synthesis. Trisaquohexakis(propionato)-μ_3-oxotriruthenium-(III,III,III) propionate, $[Ru_3O(O_2CCH_2CH_3)_6(H_2O)_3](O_2CCH_2CH_3)$, was prepared as modified by Bilgrien.[44] A mixture of 50 mL propionic acid, 50 mL ethanol, and 1.2 g NaOH were warmed under N_2 until the NaOH dissolved. Two grams of "$RuCl_3 \cdot x(H_2O)_3$" were added and the solution refluxed under nitrogen for four hours until deep green-black. The solution was cooled to -78 °C for 3-4 hours and filtered

to remove impurities including excess sodium propionate and NaCl. The filtrate was evaporated on a rotary evaporator and vacuum dried 12 hours at 50 °C to give the crude catalyst.

For chromatography on the Sephadex column as described by Bilgrien, 1 g of crude trimer was dissolved in 100 mL of methanol and chromatographed in approximately 25 mL fractions. The middle, blue green fraction was collected, discarding the first and third "bands," stripped of solvent, and rechromatographed in smaller (5 - 10 mL) fractions . This treatment yielded a product whose spectra matched the reported data. Again, the presence of trace nitrogen in the elemental analyses of this complex is an enigma. Interestingly, commercial $RuCl_3 \cdot x(H_2O)$ from Aldrich also analyzes for trace nitrogen, while "pure" $RuCl_3 \cdot x(H_2O)$ from Johnson Matthey does not. Using $RuCl_3$ from Johnson Matthey eliminates the trace nitrogen in the analyses as shown in the table below. It should be noted that commercial $RuCl_3$ is an ill-defined, heterogeneous mixture of mono- and polymeric ruthenium complexes, including oxochloro, hydroxochloro, and occasional nitrosyl complexes. The average oxidation state is closer to Ru(IV) than Ru(III), and the main constituent of $RuCl_3 \cdot xH_2O$ is considered to be a $Ru(OH)Cl_3$ species.[102] Although this does not definitively isolate the source of the nitrogen in the analyses, this data leads to the conclusion the nitrogen is most probably inherent in the starting material and is carried through the reaction.

Table 2-3

Elemental Analyses

	%C	%H	%N
theoretical for $[Ru_3O(prop)_6(H_2O)_3](prop)$	28.49	4.68	0.00
Chromatographed (Aldrich)	27.89	4.29	0.50
crude trimer (Aldrich)	29.63	4.65	0.57
crude trimer (Johnson Matthey)	28.33	4.34	0.00
theoretical for $RuCl_3 \cdot x(H_2O)$	0.00	2.29	0.00
Aldrich $RuCl_3 \cdot x(H_2O)$	0.75	2.16	0.79
Johnson Matthey $RuCl_3 \cdot x(H_2O)$	0.24	1.62	0.00

Tris(pyridine)hexakis(propionato)-μ_3-oxotriruthenium-(III,III,III) hexafluorophosphate, $[Ru_3O(O_2CCH_2CH_3)_6(C_5H_5N)_3](PF_6)$, was prepared using a modification of Wilkinson's procedure.[33] Crude $[Ru_3O(prop)_6(H_2O)_3](prop)$, (.79 g) was dissolved in 5 mL methanol, 2.5 mL of pyridine was added, and the solution was stirred for 1 hour. A solution of 1 g $NaPF_6$ in 1 mL methanol was added to the mixture and the resulting solution stored at -40 °C for 48 hours. Dark blue crystals were filtered from the cold solution, washed three times with diethyl ether, and dried under vacuum at room

temperature for 12 hours. The IR and UV-visible of this complex matched the reported values. Calculated for $[Ru_3O(O_2CCH_2CH_3)_6(C_5H_5N)_3](PF_6)$: %C = 34.77, %H = 3.95, %N = 3.69; Found %C = 33.86, %H = 3.86, %N = 3.51.

CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF A NOVEL TRINUCLEAR CARBOXYLATE COMPOUND

Background

Although trinuclear metal carboxylate complexes have been widely studied (as mentioned in Chapter I), little variation in the nature of the bridging carboxylate ligands has been attempted. The literature reports only two examples where trinuclear carboxylates have been synthesized using ligands other than alkyl carboxylates - a ruthenium trimer having dichloroacetate ligands[103] and more recent reports detailing the synthesis of Fe, Cr, and V trifluoroacetates.[104,105] The lack of such reports, especially for the ruthenium complexes, most probably stems from Wilkinson's failure to prepare the trifluoroacetate derivative of the $[Ru_3O(O_2CR)_6(L)_3]^n$ system.[33]

As reported in the last chapter, a variety of complexes having the basic structure $Ru_3O(O_2CR)_6L_3^n$ are catalysts for the selective oxidation of alcohols employing molecular oxygen as the oxidant. However, $Ru_3O(prop)_6(H_2O)_3^+$ did not catalyze the reaction of O_2 with norbornene, even after 48 hours of reaction time. This failure prompted an investigation into routes to a selective olefin epoxidation catalyst of this general type. Initial attempts centered around creating a catalyst containing fluorinated

carboxylate ligands, thus increasing the acidity of the metal centers and making the metals more likely to bind an olefin. Binding the substrate directly to the metal would also provide a method of selectively oxidizing the substrate to the desired product.

Previous work in our laboratory[106] had shown $Rh_2(OAc)_4$ to have a much lower acidity than $Rh_2(tfa)_4$, primarily due to the differences in the electronic nature of the carboxylate ligand. Doyle and others[107-109] extended these observations to the area of olefin binding. These workers showed that $Rh_2(tfa)_4$ will bind olefins while $Rh_2(OAc)_4$ will not, and studied the stability constants for these reactions. Also, the fluorinated ligands should be harder to oxidize, making the Ru(III) center a better oxidant. In light of these discoveries, the exchange of fluorinated for non-fluorinated carboxylate ligands in the $Ru_3O(prop)_6(H_2O)_3^+$ system would be an interesting extension of the previous studies.

Heptafluorobutyric acid (pfb acid) was chosen as the exchange medium due to Doyle's reports[108] that the perfluorobutyrate rhodium dimer bound olefins three times better than the trifluoroacetate complexes, as well as the fact Wilkinson was unsuccessful[33] in his attempts to perform this exchange with trifluoroacetic acid. The method used was an adaptation of a previously reported synthetic route for the conversion of $Rh_2(OAc)_4$ to the trifluoroacetate analogue.[106] A typical synthesis involved refluxing crude $Ru_3O(prop)_6(H_2O)_3^+$ in a 10:1 mixture of pfb acid and pfb anhydride, stripping away the solvent, and dissolving the residue in diethyl

ether. The solution was then filtered and evaporated, leaving dark black crystals which were dried in vacuo for 12 hours at 50 °C.

Characterization

Several spectroscopic methods were used to identify the nature of this complex. FTIR showed a decided difference between this complex and the starting propionate trimer (Figures 3.1 and 3.2). The water absorbance at 3400 cm^{-1} is absent, and the ν_{CO} stretch has shifted from 1567 to 1704 cm^{-1}. Other significant differences occur as well in the CH_3 and CF_3 regions. As a reference, the ν_{CO} stretch for neat perfluorobutryic acid occurs at 1774 cm^{-1}.

Proton NMR, shown in Figures 3.3 and 3.4, indicate the absence of the distinctive peaks representative of the starting material. The resonances observed are undoubtedly due to a slight impurity, either in the complex or the solvent since they cannot be attributed to either coordinated ether or residual starting material. Fluorine NMR, on the other hand, gives the expected splitting pattern for a trinuclear carboxylate containing both bound and ionic carboxylates (Figure 3.5). The resonances are broadened slightly at the base, indicative of the paramagnetism of the Ru_3O core. Again, as a comparison, the free acid gives rise to three resonances at 82.5, 121, and 128 ppm. The relative insolubility of the complex, combined with parameters inherent to the program used to transform the data and the presence of fluorine-containing polymers in the probe, make precise integration virtually impossible. The best integrated ratios obtained were 16:3, 11:2, and 10:2, not

Figure 3.1 FTIR of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ in KBr.

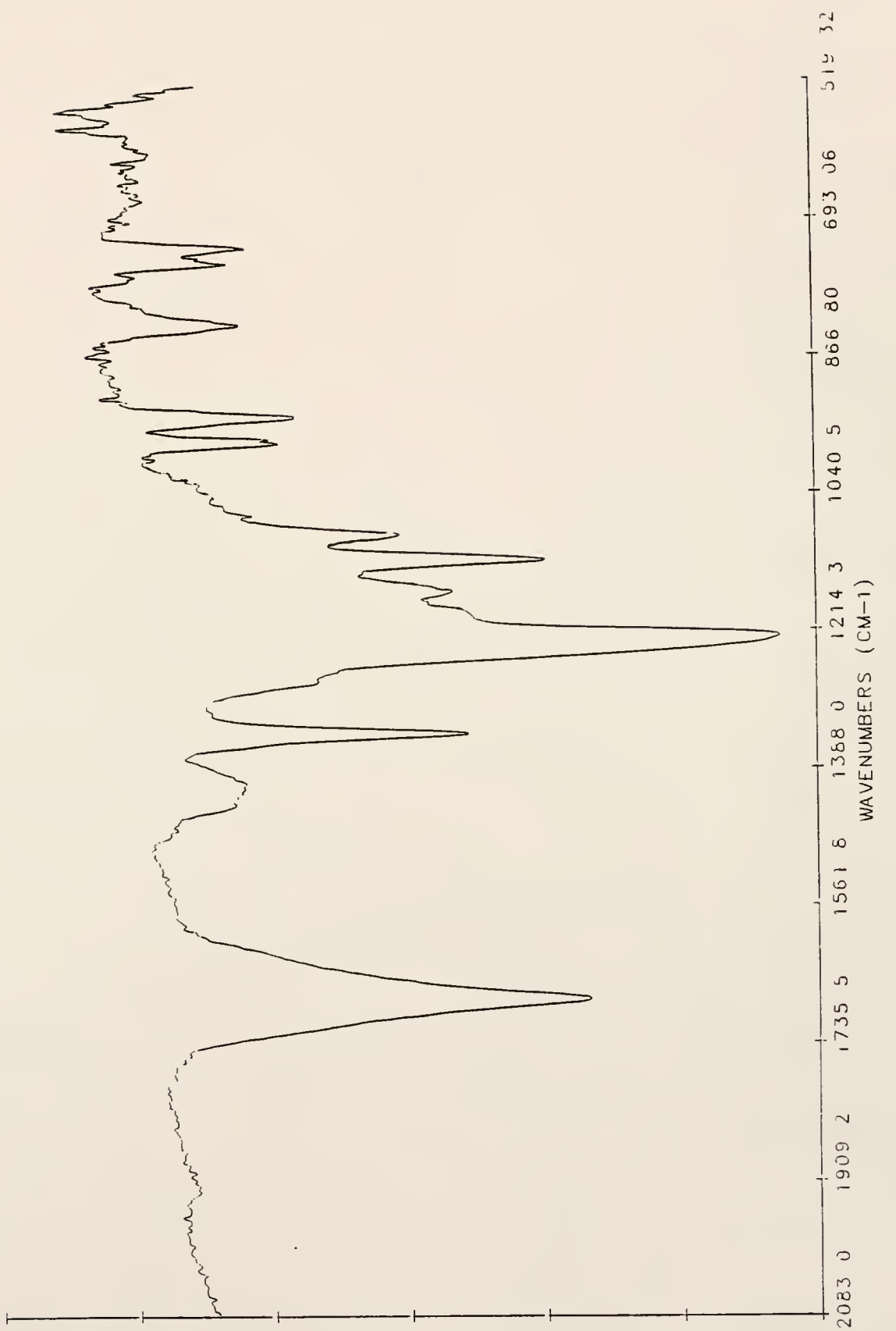
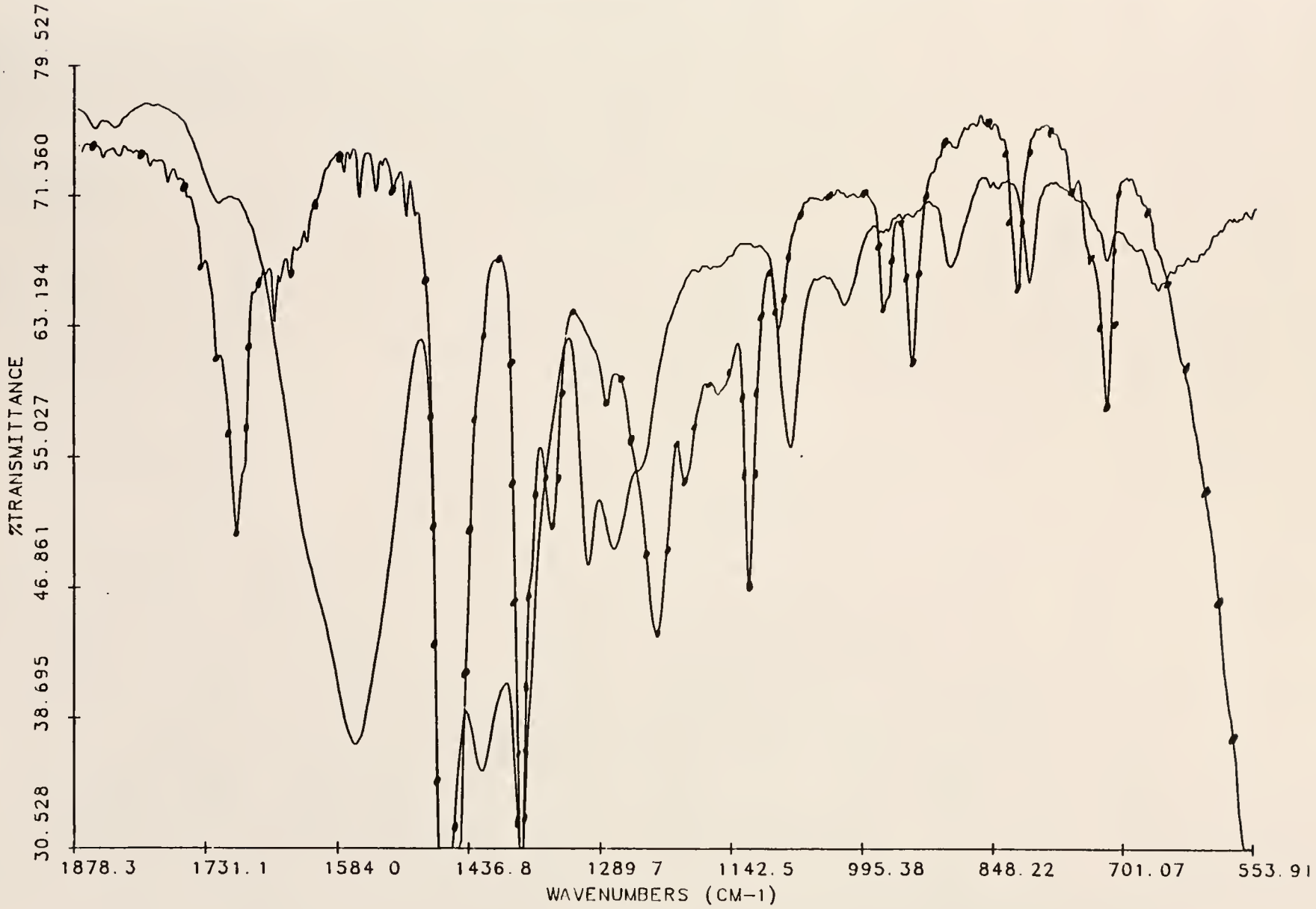

2083 0
1909 2
1735 5
1561 8
1388 0
1214 3
1040 5
866 80
693 06
519 32
WAVENUMBERS (CM-1)

Figure 3.2 FTIR overlay of $[Ru_3O(prop)_6(H_2O)_3](prop)$ (———) and $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (-•—•—•-) as Nujol mulls.


%TRANSMITTANCE
79.527
71.360
63.194
55.027
46.861
38.695
30.528
1878.3
1731.1
1584 0
1436.8
1289 7
1142.5
995.38
848.22
701.07
553.91
WAVENUMBERS (CM-1)

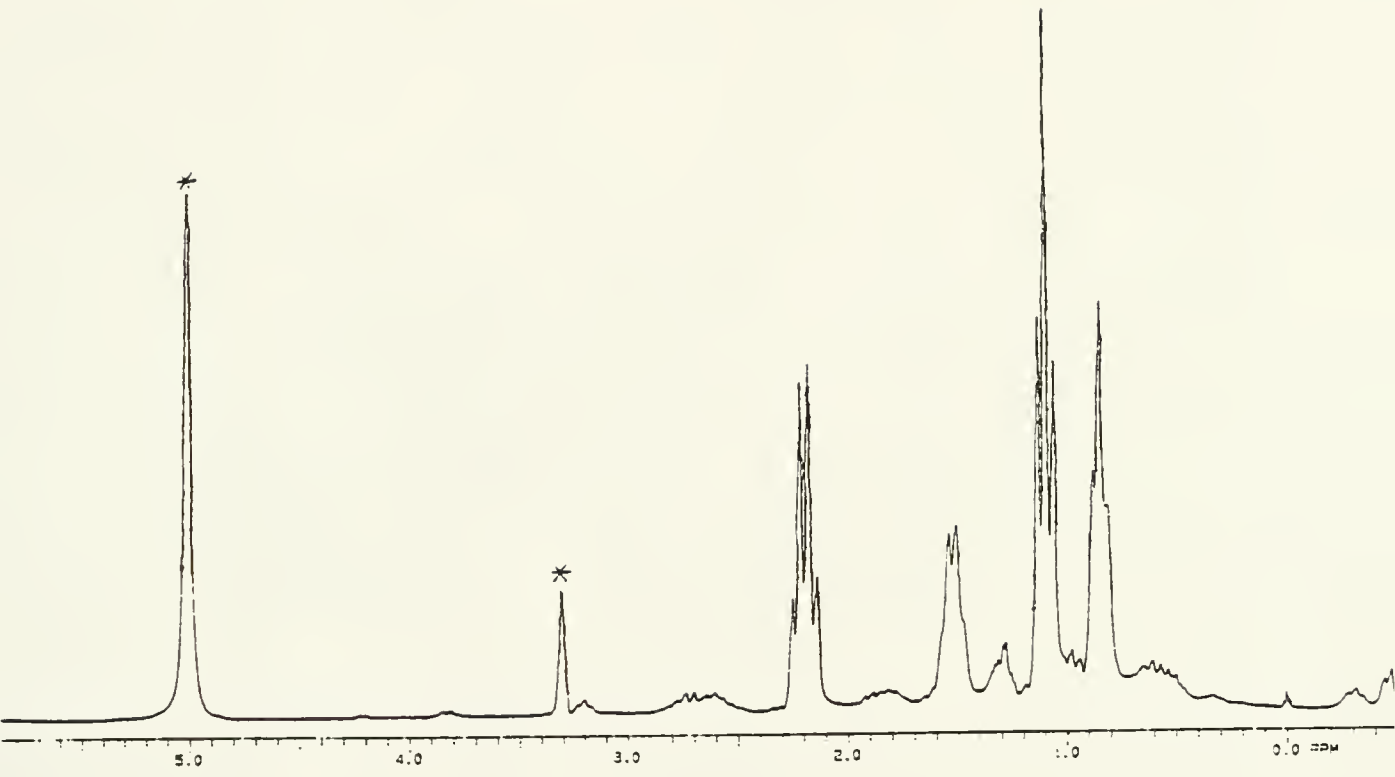


Figure 3.3 ^{1}H NMR of crude $[Ru_3O(prop)_6(H_2O)_3](prop)$ in CD_3OD. An * marks residual solvent peaks.

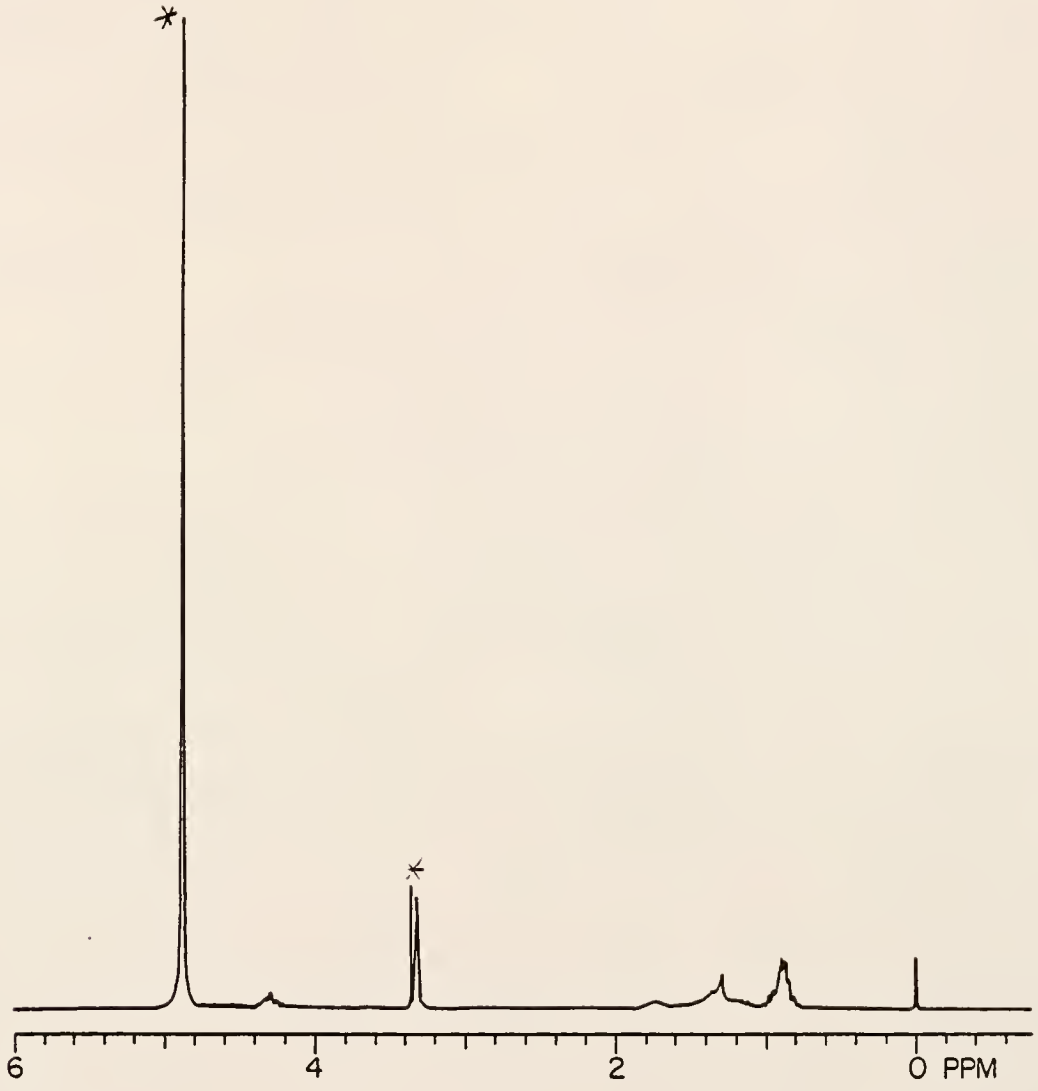
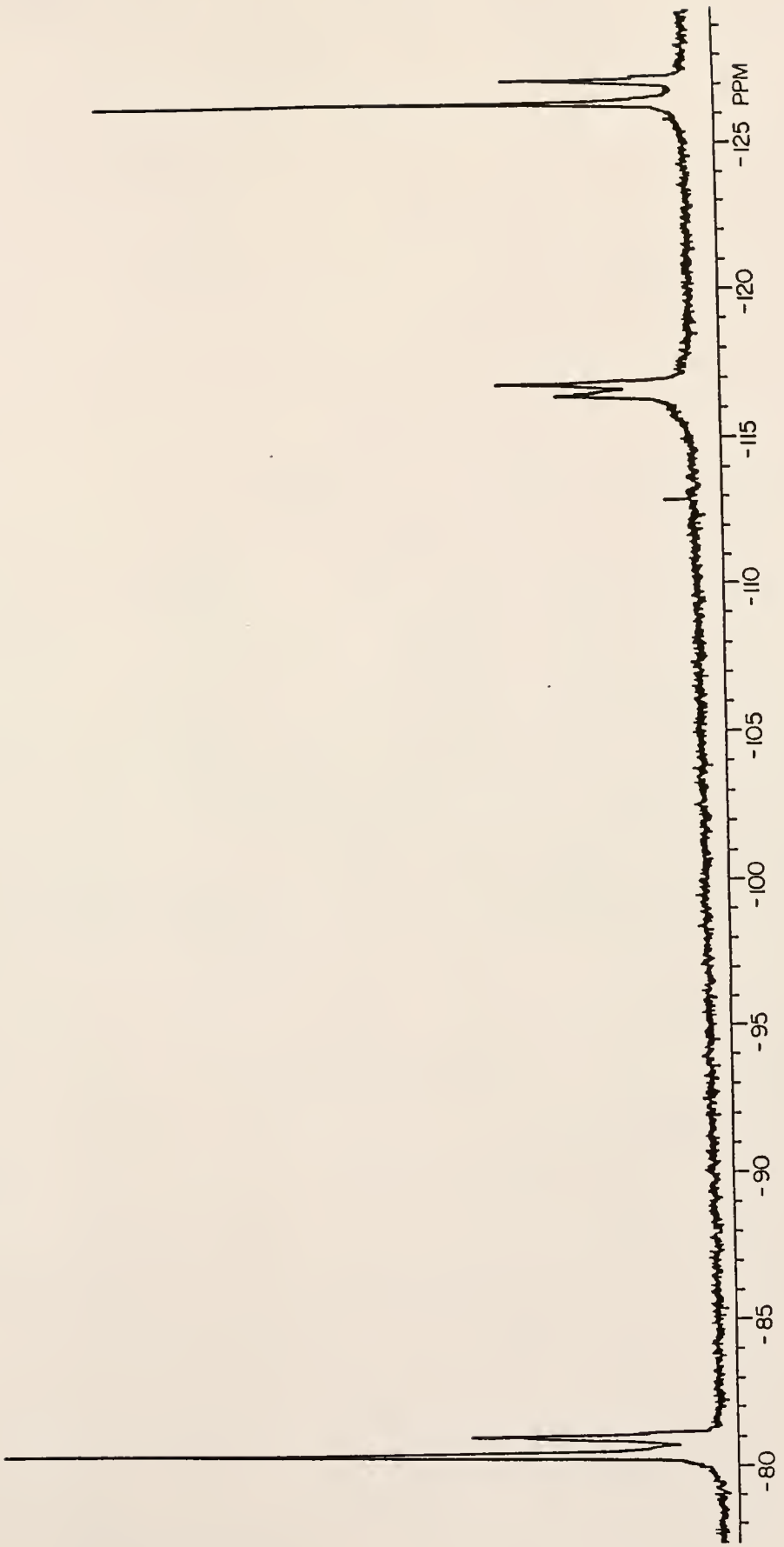


Figure 3.4 ^{1}H NMR of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ in CD_3OD. An * marks residual solvent peaks.

Figure 3.5 ^{19}F NMR of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ in CD_3OD.


-125 PPM
-120
-115
-110
-105
-100
-95
-90
-85
-80

significantly different from the 6:1 ratio that would be expected for a complex having the formula $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

The UV-visible spectrum of the perfluorobutyrate complex shows a similar shift with the absorbances at 610 and 670 nm (of the original complex) moving to 575 and 760 nm. A new absorbance appears at 950 nm as well (Figure 3.6). As further evidence for the existence of the trinuclear species, a titration with pyridine shows distinct changes in the spectrum upon the addition of three equivalents of base (Figures 3.7 and 3.8). The shoulder of the charge-transfer band at 375 shifts to 415 nm with a subsequent decrease in intensity (ϵ = 2500). The peak at 575 becomes more distinct as well. These peaks and shoulders, along with the epsilon values, are given in Table 3.1, as are other spectral data of interest from IR and NMR spectra.

Molecular weight determinations using the Signer method[110] were quite unsuccessful. Even after 3 weeks of equilibration, a constant volume for the complex solution was not obtained, indicating the complex was probably not stable in solution over extended periods of time. Hovever, FAB mass spectroscopy, a useful technique for obtaining molecular weights of materials having a high molecular weight, gave a parent ion peak at 1675 mass units, corresponding to a protonated $Ru_3O(pfb)_6(Et_2O)_3$ species. Other significant peaks in the mass spectrum correspond to the successive loss of coordinated ether and pfb ligands. (Figures 3.9 and 3.10). Elemental analysis data further supports the proposed structure of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$. Analysis by Galbraith Laboratories gave

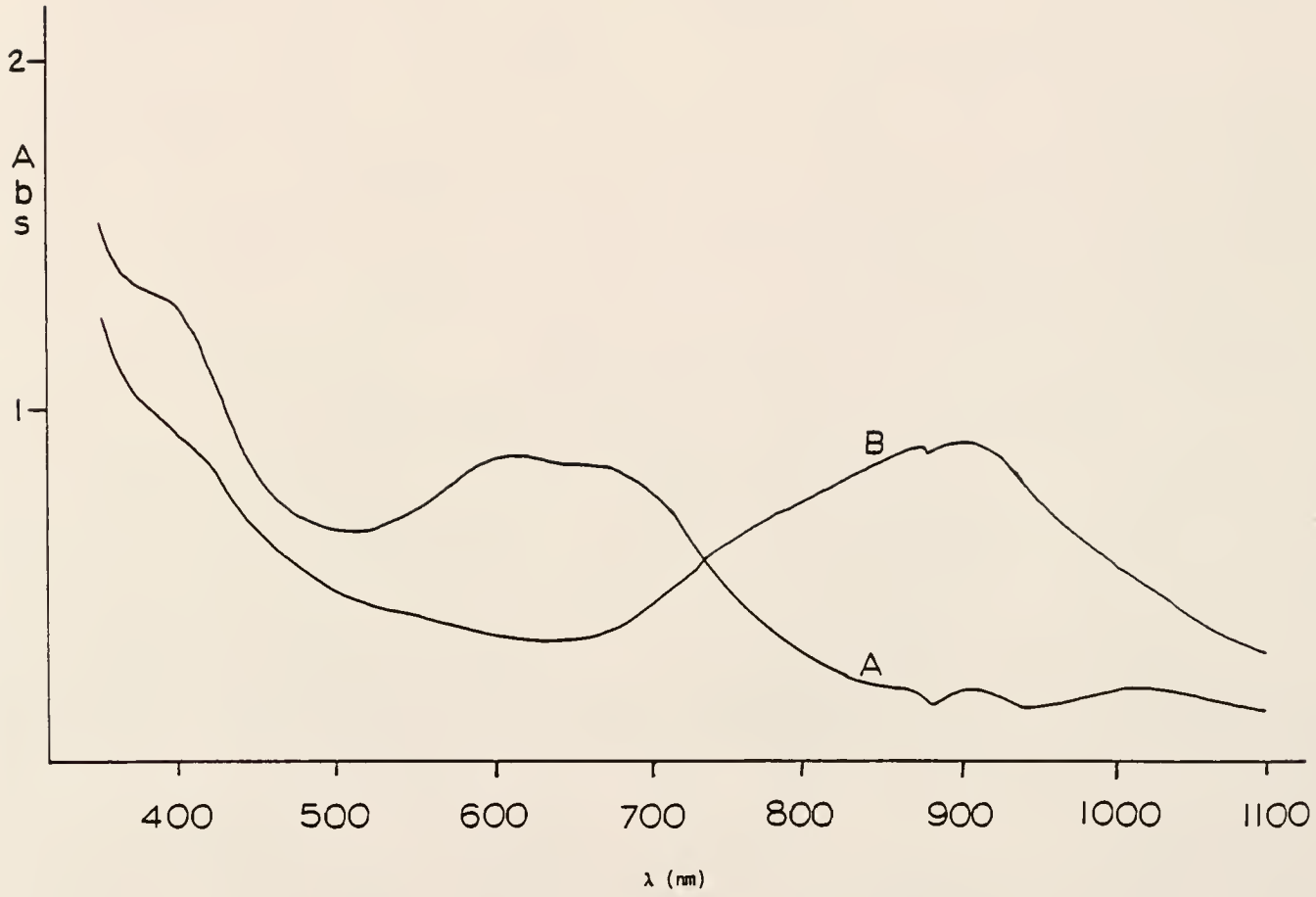
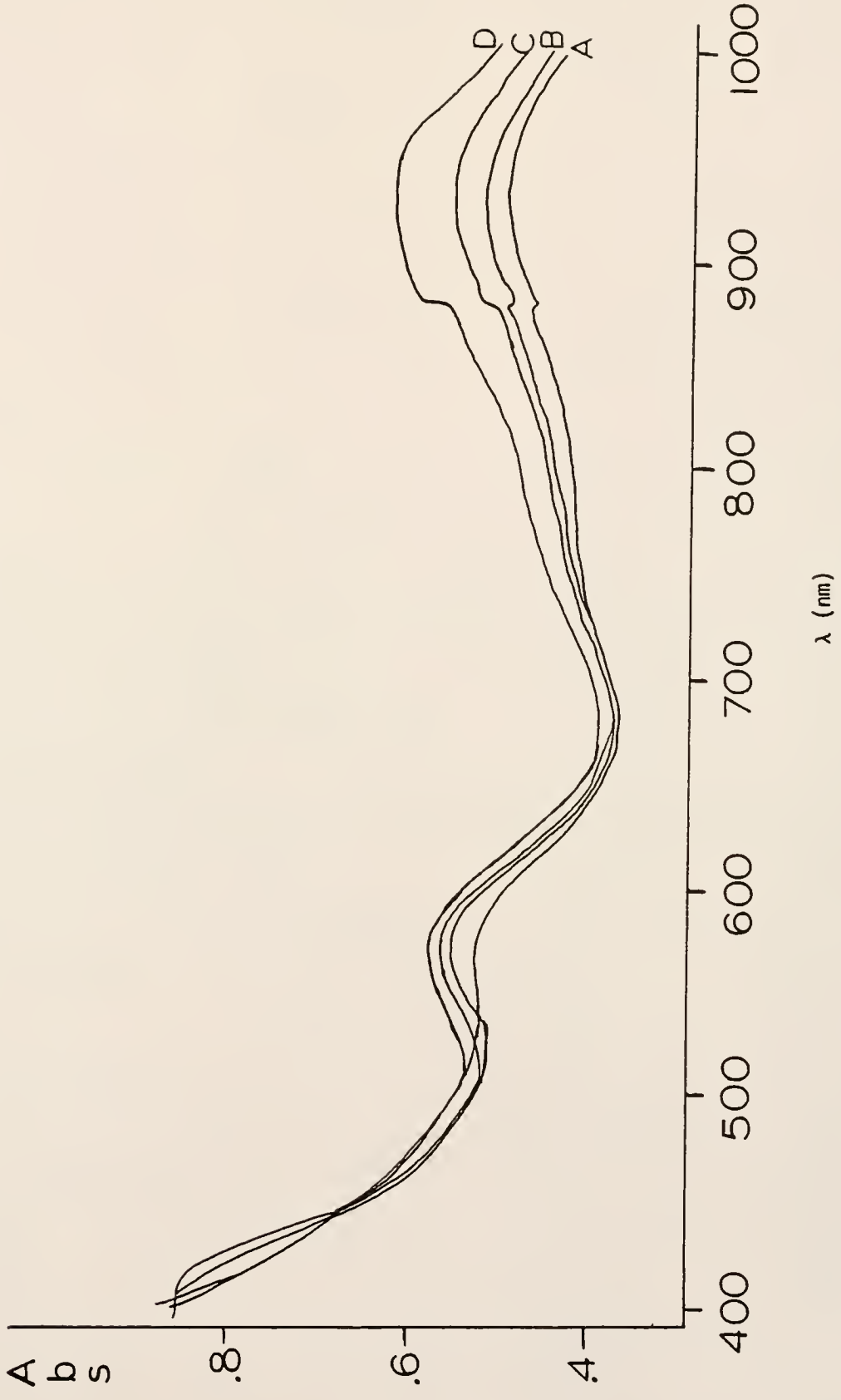


Figure 3.6 UV-Vis overlay of (A) $[Ru_3O(prop)_6(H_2O)_3](prop)$ and (B) $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ in methanol.

Figure 3.7 UV-Vis titration of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ in acetonitrile with pyridine. (A) $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (B) one equivalent of pyridine (C) two equivalents of pyridine (D) three equivalents of pyridine.


Abs
.8
.6
.4
400
500
600
700
800
900
1000
λ (nm)
A
B
C
D

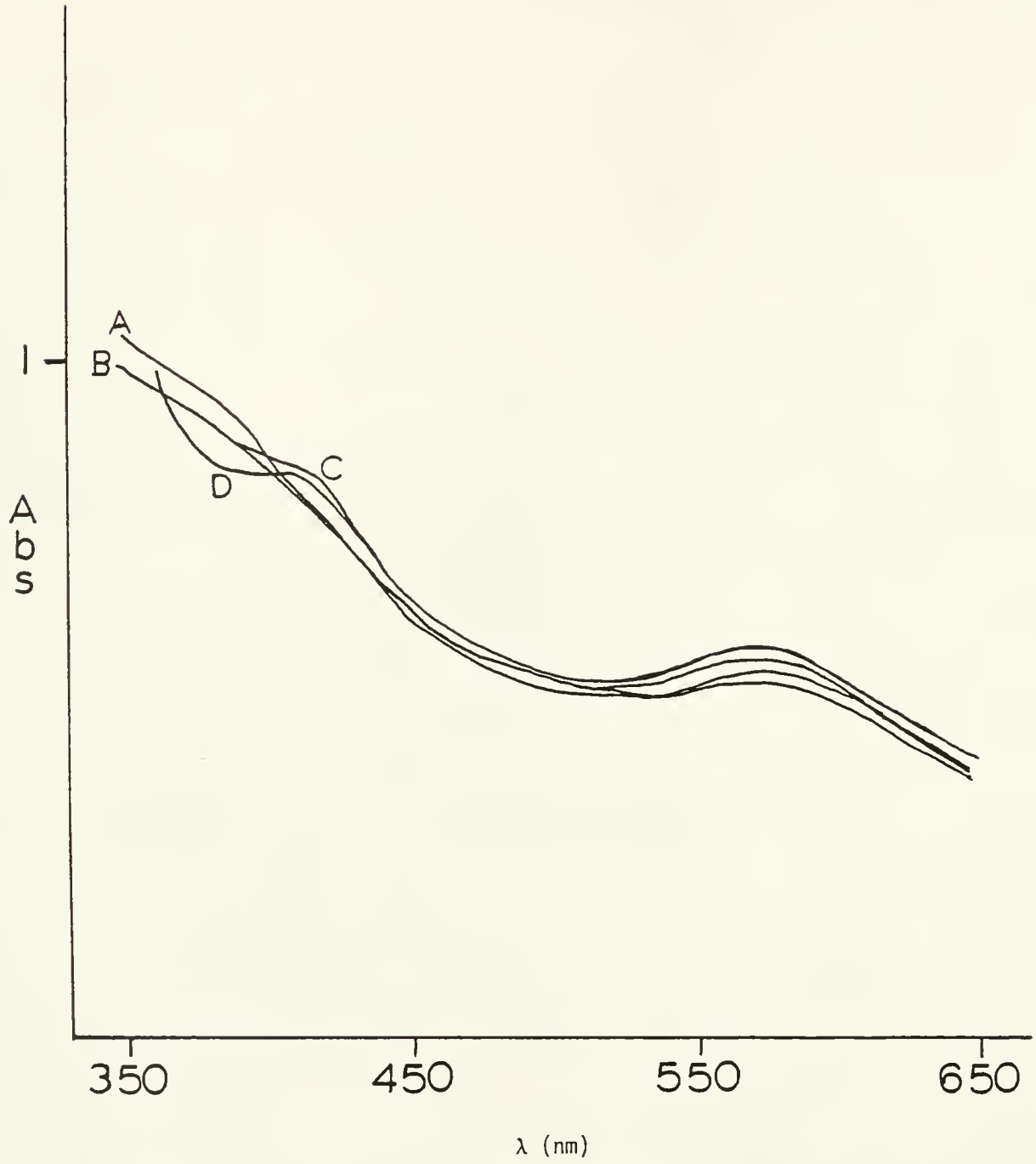


Figure 3.8 Expansion of the UV-vis titrations with pyridine. (A) $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (B) one equivalent of pyridine (C) two equivalents of pyridine (C) three equivalents of pyridine.

Table 3.1

Spectral Data for
$[Ru_3O(pfb)_6(Et_2O)_3](pfb)$

^{19}F NMR (referenced to internal $CFCl_3$ at 0 ppm)

80.8	81.2 (triplet)
116.7	117.4 (quartet)
126.7	127.2 (singlet)

FTIR (Nujol mull)

1704(s)	974(m)
1342(m)	936(m)
1224(s)	821(m)
1120(s)	

UV-Vis

nm	ϵ
375 (sh)	3383
575 (sh)	1574
760 (sh)	1312
950	1444

Figure 3.9 FAB positive ion mass spectrum of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

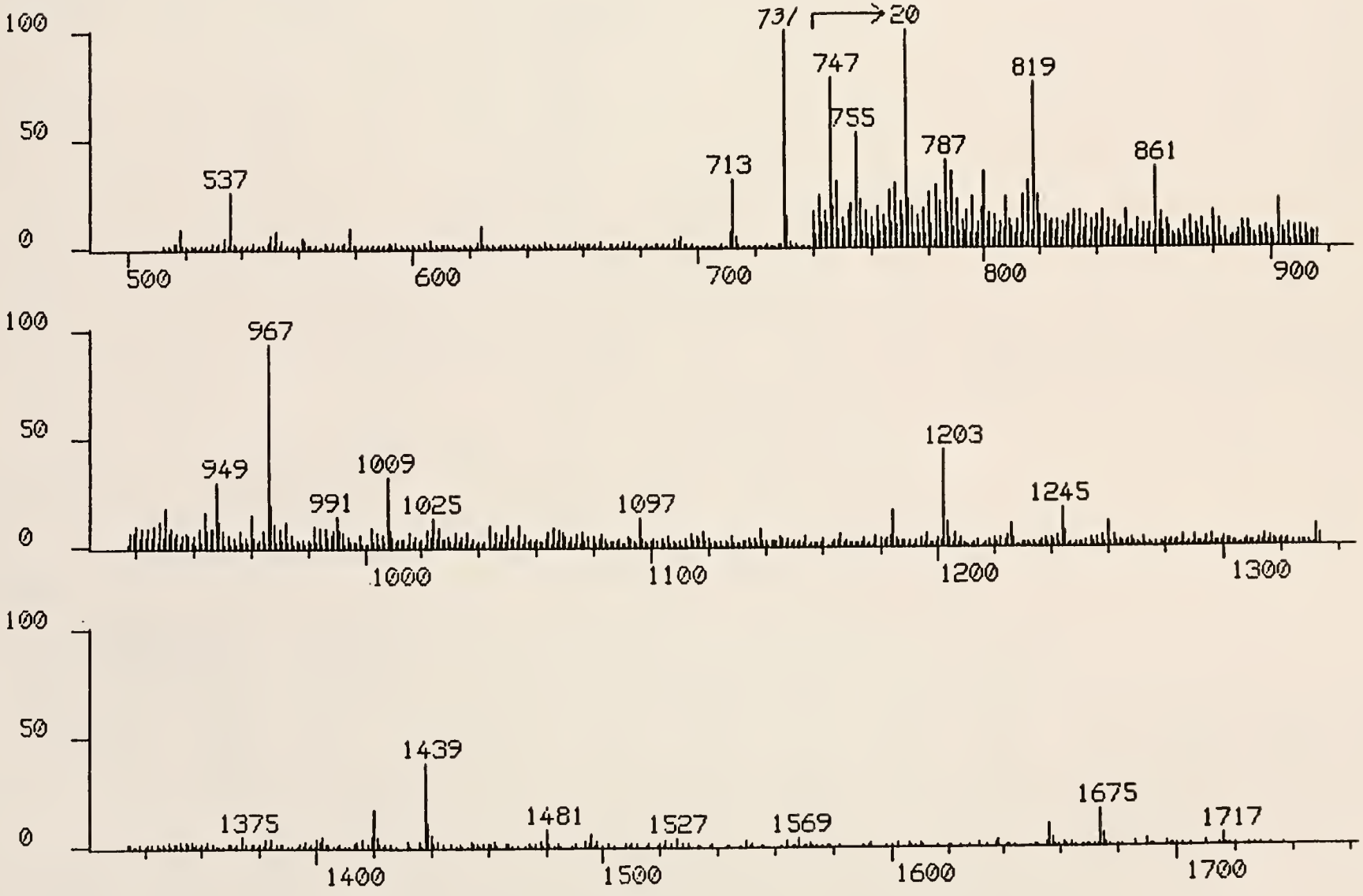
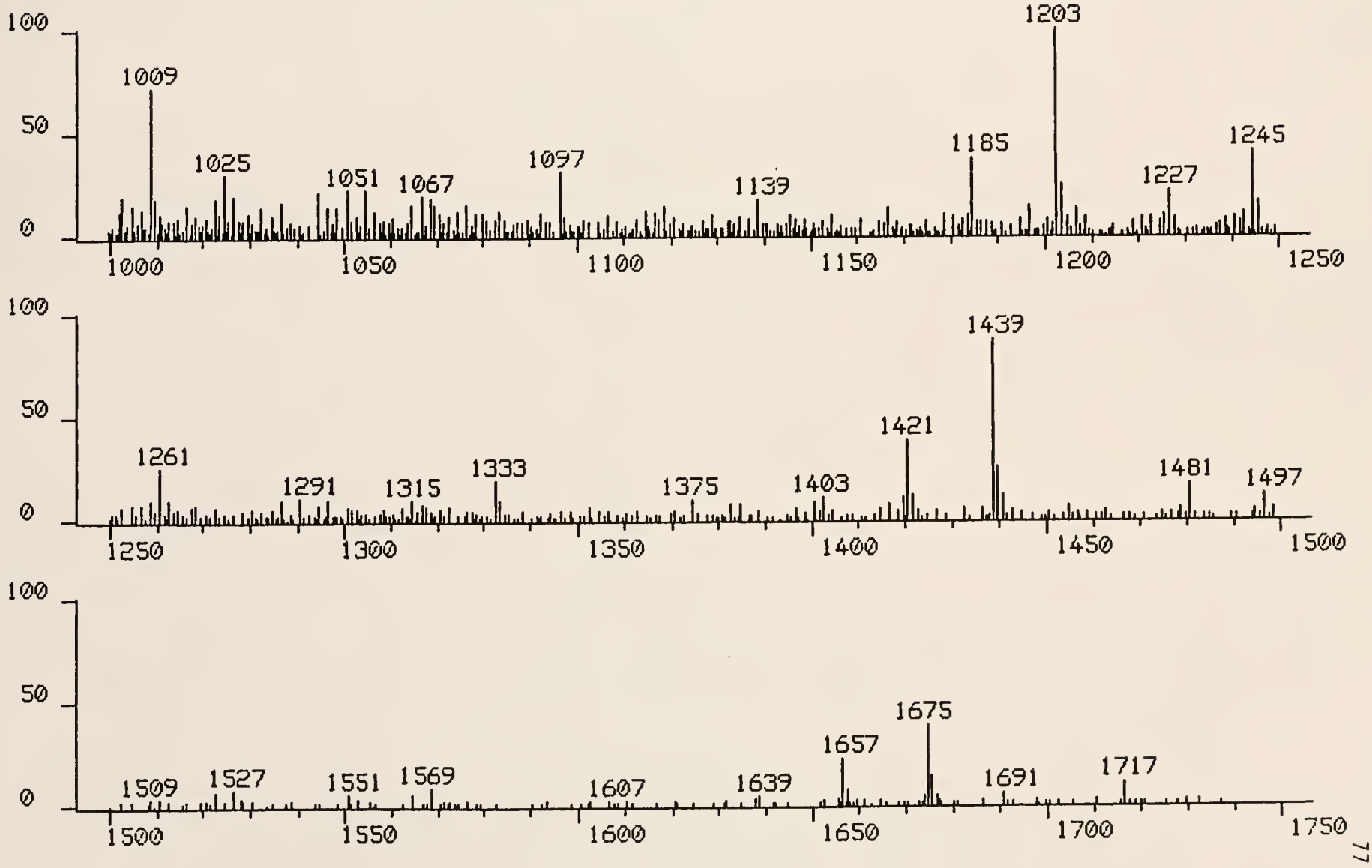

100
50
0
731
20
747
819
755
787
861
713
537
500
600
700
800
900
100
50
0
967
949
1009
991
1025
1097
1203
1245
1000
1100
1200
1300
100
50
0
1439
1375
1481
1527
1569
1675
1717
1400
1500
1600
1700

Figure 3.10 Expanded FAB mass spectrum of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.


100
50
0
1009
1025
1051
1067
1097
1139
1185
1203
1227
1245
1000
1050
1100
1150
1200
1250
100
50
0
1261
1291
1315
1333
1375
1403
1421
1439
1481
1497
1250
1300
1350
1400
1450
1500
100
50
0
1509
1527
1551
1569
1607
1639
1657
1675
1691
1717
1500
1550
1600
1650
1700
1750

%C = 21.20, %H = .73, and %F = 47.94, while values calculated for $[Ru_3O(pfb)_6(Et_2O)_{1.5}](pfb)$ give %C = 21.24, %H = .78 , and %F = 48.46.

All attempts at growing crystals suitable for X-ray analysis were unsuccessful, probably due to the highly unordered pfb ligands as well as the ready substitution of water of the ether ligands. Therefore, no definitive proof for the structure of this complex is available. However, based on the evidence presented thus far, the assumption of a complex having the formula $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ and the "basic trinuclear acetate" structure is not unreasonable. Based on this assumption, this complex was screened as a catalyst for the oxidation of several organic substrates, as will be discussed in the following chapters.

Experimental

All reagents used were reagent grade or better; the majority were readily available from Aldrich Chemical Company. FTIR spectra were collected on a Nicolet 5DXB FT spectrometer either as KBr pellets or Nujol mulls. Proton and fluorine NMR spectra were collected on either a Varian XL-200 (at 200MHz) or a Varian VXR-300 (at 300 MHz) FT spectrometers using TMS and $CFCl_3$, respectively, as internal (or external where required) standards at 0 ppm. Electronic spectra were performed on a PE 331 spectrophotometer and were background corrected in all cases. Elemental analyses were performed on a service basis by the University of Florida microanalytical laboratory or by Galbraith Laboratories (Knoxville, TN). Mass spectral determinations were carried out at the Middle

Atlantic Mass Spectrometry Laboratory at Johns Hopkins University, a National Science Foundation Shared Instrument Facility.

Synthesis

Tris(etherato)hexakis(heptafluorobutyrato)-μ_3-oxotriruthenium (III,III,III) heptafluorobutyrate: $[Ru_3O(O_2CCF_2CF_2CF_3)_6(Et_2O)_3](O_2CCF_2CF_2CF_3)$.

Crude $Ru_3O(prop)_6(H_2O)_3^+$ was prepared as described in the previous chapter. The exchange was carried out by dissolving .5 g of the crude propionate trimer in a mixture of 10 mL heptafluorobutyric acid and 1 mL heptafluorobutyric anhydride. The deep green solution gradually changed to an olive-brown color upon refluxing under N_2 for 90 minutes. The mixture was filtered warm and evaporated, leaving a dark black, gummy solid. This solid was dissolved in 75 mL diethyl ether, filtered and evaporated; this process was repeated twice. The final solid, obtained as a black powder, was dried *in vacuo* at 50 °C for 12 hours. Calculated for $[Ru_3O(O_2CCF_2CF_2CF_3)_6(Et_2O)_{1.5}](O_2CCF_2CF_2CF_3)$: % C = 21.24, % H = 0.78, % N = 0.0, % F = 48.46. Found (Galbraith Laboratories) % C = 21.20, % H = 0.73, % F = 47.94. Found (U. of F. Laboratories) % C = 20.91, % H = .12, % N = .11. This complex is highly hygroscopic, in humid weather becoming quite gummy, and was stored in a desiccator.

CHAPTER IV

OLEFIN OXIDATIONS BY A NOVEL TRINUCLEAR RUTHENIUM CARBOXYLATE COMPLEX

Introduction

The oxidation of hydrocarbons to a variety of oxygen-containing organic chemicals is a highly useful industrial transformation as outlined in Chapter I. Olefinic substrates were investigated initially by the rubber industry as autoxidation substrates,[4] which led ultimately to the current process for the epoxidation of ethylene and the Wacker process. Currently, the lack of a feasible liquid-phase process for the epoxidation of propylene has generated a great deal of interest in the selective oxidation of olefins.[111]

Ethylene and propylene are commercially inviting substrates for study, due to the demand for their respective epoxides for plastics, solvents, antifreeze, and other chemicals, The epoxidation of ethylene over a silver-alumina catalyst is a unique, well-studied heterogeneous system, and will not be further discussed.[6,52,112] Propylene, on the other hand, cannot be oxidized to the epoxide under similar conditions and is currently epoxidized using a molybdenum-catalyzed process involving alkyl hydroperoxides.[6,111]

Asymmetric epoxidations have received a great deal of attention in the literature due to Sharpless' discovery that chiral titanium-

isopropoxide complexes catalyze the epoxidation of allylic alcohols.[113-117] Epoxides formed in this fashion are generally greater than 95% enantiomerically pure. This process has been licensed by Aldrich Chemical Company and can be used to prepare intermediates for a host of natural products of interest to the pharmaceutical industry.[118]

Oxometal reagents containing most commonly the metals molybdenum or vanadium, generally in combination with peroxides or hydroperoxides, have been shown to actively epoxidize olefins.[8] A great deal of controversy concerning the mechanism of the peroxomolybdenum-catalyzed epoxidation of olefins still exists. Both Sharpless and Mimoun mechanisms are referred to for these and similar oxidations.[3,8,119,120] Ruthenium compounds, on the other hand, have long been used to cleave double bond in organic chemistry. Ruthenium tetroxide in combination with an oxygen source, is a powerful reagent for cleaving carbon-carbon double bonds to produce ketones or carboxylic acids.[8] The well-studied, widely-used $RuCl_2(PPh_3)_3$ has also been shown to selectively oxidize cyclohexene to the allylic ketone with O_2 and styrene to styrene oxide.[119,121] Selective epoxidation by ruthenium compounds is much harder to achieve, however.

Reports of ruthenium complexes catalyzing a variety of olefin oxidations using oxygen-atom transfer reagents such as iodosobenzene instead of O_2 abound. Commercially available ruthenium trichloride, bipyridyl, and periodate in a biphasic solvent selectively oxidized olefins to epoxides.[122] An electrogenerated compound thought to be

$[Ru^{V}(N_4O)(O)]^{2+}$ (where N_4O is bis[2-(2-pyridyl)ethyl][2-oxy-2-(2-pyridyl)ethyl]amine) is reported to be the active species for the epoxidation of olefins as well using oxygen-atom transfer reagents.[123]

In contrast, only a few ruthenium compounds catalyze the selective oxidation of olefins with molecular oxygen. The epoxidation of norbornene was achieved with O_2 using several Ru(II) catalysts.[124] This reaction was only about 10% selective to the epoxide, generating oligomers of norbornene via a ring-opening process as well as small amounts of norbornanone.

Metalloporphyrins have received a great deal of attention as researchers try to mimic and understand the activities of biological systems like cytochrome P-450.[125] Iron and manganese prophyrins have especially been used as probed for this system and will epoxidize alkenes with oxygen atom transfer reagents.[126-130] Recently a ruthenium porphyrin utilizing molecular oxygen as the oxidant has been prepared by Groves and coworkers.[131,132] A hindered <u>trans</u>-dioxo ruthenium(VI) porphyrin complex, at ambient temperature and 1 atm O_2, will react, albeit slowly, with a variety of olefins to form epoxides. A similar compound, $[Ru(O)_2(dmp)_2](PF_6)_2$, where dmp = 2,9-dimethyl-1,10-phenanthroline, has been shown by Bailey and Drago to epoxidize olefins under slightly more stringent conditions -- 55 °C and 3 atm O_2.[133] Another dioxoruthenium(VI) complex containing acetate and pyridine ligands will oxidize cyclohexene, hexene, and styrene slowly, presumably via oxygen atom transfer.[134]

Meyer, in his extensive studies of ruthenium polypyridyl complexes, has found a Ru(IV)-oxo complex will stoichiometrically or electrocatalytically oxidize a variety of substrates including olefins.[95,135,136] In general, high-valent ruthenium oxo complexes have been studied intensively since the proposal that high valent metal-oxo species are the active intermediates in metalloporphyrin oxidations.

In light of the recent successes of ruthenium complexes as olefin epoxidation catalysts, attempting to use the ruthenium carboxylate trimers to oxidize olefins would be an intriguing extension of the alcohol oxidation system encountered in Chapter II. The use of such complexes as catalysts was indeed the primary justification for the synthesis and characterization of the novel perfluorobutyrate complex outlined in Chapter III.

Initial tests of the catalytic activity of the new ruthenium perfluorobutyrate trimer were carried out using n-propanol as the substrate. Under standard reaction conditions (see Chapter II), no oxidation occurred after 12 hours of reaction time. The exchange of alkyl for fluorinated carboxylate ligands was designed to increase the ability of the metal centers to bind olefins, however.

Attempting to validate the assumption the perfluorobutyrate complex would catalyze the epoxidation of olefins, a number of olefins were tested with this complex (Table 4-1). Unfortunately, the goal of selectively oxidizing olefins was not realized, since the ruthenium perfluorobutyrate complex actively initiates the free radical autoxidation of all of the substrates attempted.

Table 4.1

Olefin Substrates[a]

Substrate	product	mmoles	turnovers[b]
cyclohexene	2-cyclohexene-1-ol	1.37	67 / 3 hrs
	2-cyclohexene-1-one	.764	38 / 3 hrs
	cyclohexene oxide	.336	17 / 3 hrs
norbornene	norbornene oxide:	.055	4 / 24 hrs
	(exo-2,3-epoxy-norbornane)	.302	22 / 24 hrs
trans-β-methylstyrene	benzaldehyde	.325	3 / 48 hrs
	acetaldehyde	c	
	trans epoxide: (1R,2R-(+)-1-phenyl-propylene oxide)	trace	
hexamethyl-Dewarbenzene	hexamethylbenzene (major)	c	
	hexamethylbenzene oxide (minor)	c	

a) Reaction conditions are slightly different from reaction to reaction. Specific details can be found under "Scope of Catalysis."

b) Turnovers = moles of product/moles of catalyst used in the specified time.

c) Not quantified

Scope of Catalysis

The general setup and apparatus used are the same as described in Chapter II under "Scope of Catalysis." For the olefin oxidations, the temperature was held constant at 65 °C; all reactions were performed under 40 psi O_2 initial pressure. Except where otherwise noted, the solvent used was acetonitrile, and in all cases a minimum 100-fold excess of substrate was used. All reactions were monitored via GC or CG/MS. The procedure used varied depending upon the state of the substrate. For norbornene, a solid, the substrate was dissolved in 50 mL acetonitrile in the pressure bottle and placed in the oil bath. Upon dissolution of the solid, the catalyst was added and the apparatus assembled. No preliminary preparation of norbornene was necessary; however, for some of the liquid substrates used, pretreatment by washing through a neutral alumina column to remove peroxides was required. In the case of cyclohexene, a 20% by volume solution in acetonitrile (10 mL substrate/40 mL solvent) was used; the other reactions were carried out using 2 mL substrate in 50 mL solvent. No internal standard was used in any of these reactions except 2-octanone in the cyclohexene oxidation. In general, approximately 20 mg of catalyst was used, corresponding to 10^{-5} moles. Products were determined by GC using a DEGS column and FID detector. The amounts of products were determined from a calibration curve relating moles of products to relative area percents as described in Chapter II.

Results and Discussion

The oxidation of cyclohexene was attempted first, since it is one of the easiest substrates to oxidize.[3] After an induction period of one hour, virtually all of the products typical of a free radical autoxidation process were observed. The major products, cyclohexene oxide, 2-cyclohexene-1-ol, and 2-cyclohexene-1-one, were formed in roughly a 4:16:9 molar ratio after 3 hours. Significant amounts of other products (approximately 10) were also observed but not quantified. The addition of benzoquinone, a free radical trap, inhibited the reaction for a finite period (between 6 and 9 hours, depending on the amount of benzoquinone added), after which the reaction resumed. Presumably, oxidation of the alkene resumes after the oxidation of the quinone is complete.

At the other end of the spectrum in terms of oxidizability lies norbornene. This substrate is widely used to prove the existence of non-radical pathways in catalytic oxidation studies, since the kinds of allylic hydrogen abstraction so prevalent in cyclohexene oxidations are not possible in norbornene. Most of the norbornene radicals produced are highly unstable, and would be expected to decompose into alcohol and ketone products, as well as epoxide. An induction period of 24 hours was observed in the oxidation of norbornene also, after which primarily norbornene oxide was produced.(Figure 4.1). This induction period is similar to that seen in the oxidations by the high-valent oxo-ruthenium complex Ru(dmp).[133] The Ru(pfb) complex was slightly less active than this previously reported catalyst, producing 22 turnovers in 48 hours as

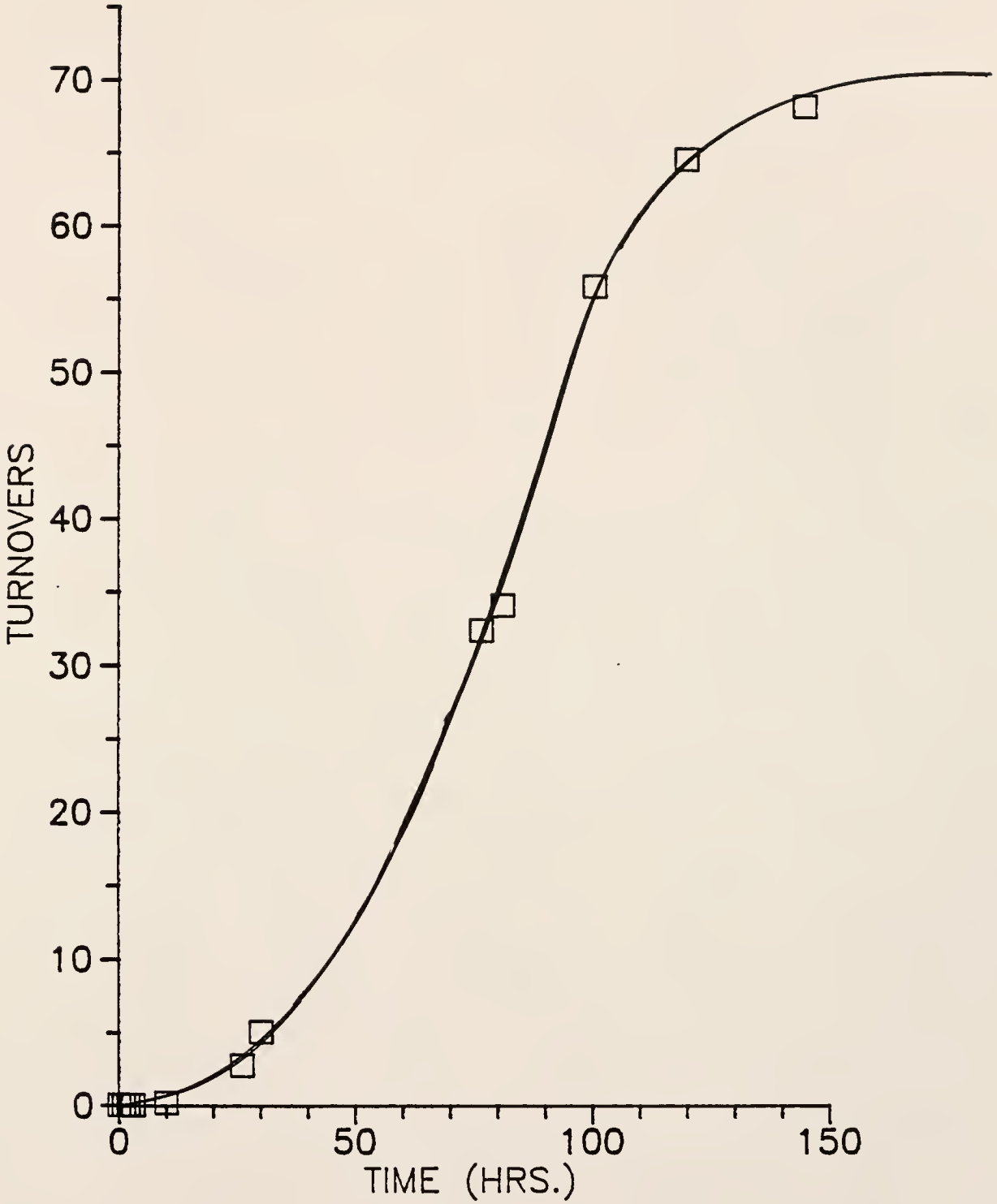


Figure 4.1 Activity curve for the oxidation of norbornene by $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

compared to 37 turnovers in the same period of time for the Ru(dmp) catalyst.

Based on this result which seemed to indicate the selective epoxidation of olefins by the Ru(pfb) catalyst, the oxidation of trans-β-methylstyrene was attempted. This substrate had previously been used by Groves to determine both the stereoselectivity and possible mechanistic pathways for olefin epoxidation by his Ru(VI) porphyrin.[132] The oxidation of trans-β-methylstyrene proceeded very slowly. Only trace amounts of the trans epoxide were produced after 40 hours of reaction time. The major products of the reaction were those due to the cleavage of the double bond--benzaldehyde and acetaldehyde--indicative of a radical process.

Obviously, the perfluorinated ruthenium trimer acts as a potent free radical initiator. Traylor, et. al, have shown that iron heme complexes (cytochrome P450 analogs) also will catalyze radical-based oxidations of alkenes.[126,127] In order to distinguish between a free radical chain mechanism and a caged radical pair, the substrate hexamethylDewarbenzene was chosen. Under Traylor's conditions, autoxidation processes produce hexamethylbenzene as product, while a caged radical pathway produces epoxide when m-chloroperbenzoic acid is used as the oxidant. At 65 °C and 3 atm O_2, however, this substrate is extremely reactive. No observable distinction in either amount of type of product formed could be made between a blank (using O_2 and no catalyst present) and a typical catalytic run. Another major disadvantage of this substrate is its sensitivity to light.[137-140] For these reasons, hexamethylDewarbenzene has limited

use as a substrate for mechanistic information in catalytic oxidation studies under these stringent conditions. However, these results do support the free radical nature of these oxidations.

These reactions show a marked solvent dependency as well (see Table 4-2). Using norbornene as the substrate, a series of reactions were run in a variety of solvents. In acetonitrile, 30 turnovers in a 48 hour period were achieved, while no reaction was observed in benzonitrile, pyridine, or nitrobenzene. Approximately 5 turnovers in 48 hours were achieved in ethanol. These results can be attributed to the increased solubility of O_2 in acetonitrile compared to the other solvents attempted. The decrease in activity in ethanol is attributed primarily to its ability to act as a free radical trap. These experiments, combined with the fact the addtion of AIBN (azo-bis(isobutyronitrile)), a free radical initiator, decreases the induction period and increases the number of turnovers achieved (from 22 to 72 in 48 hours) all indicate a free radical mechanism is involved in the oxidations (Figure 4.2). A caveat is implicit in these results as well--norbornene is not as inert to allylic hydrogen abstraction as has been previously assumed.

Observing changes in the catalyst during or after the reaction would give some insight into the role the catalyst plays in these reactions. The presence of the fluorinated ligands in the catalyst enables the fate of the catalyst to be relatively easily monitored via ^{19}F NMR. Variance in the structure of the compound, changes in oxidation state, or complete degradation of the catalyst could be discerned from changes in the resonances of the fluorinated atoms of

Table 4.2

Solvent Dependency
in Norbornene Oxidations

	Turnovers[a]	
solvent	24 hrs	48 hrs
acetonitrile	3.5	29.8
pyridine	0.0	0.0
benzonitrile	0.0	0.0
ethanol[b]	3.0	5.0
nitrobenzene	0.0	0.0

a) Turnovers = moles of product/moles of catalyst.

b) No oxidation products from the solvent were observed.

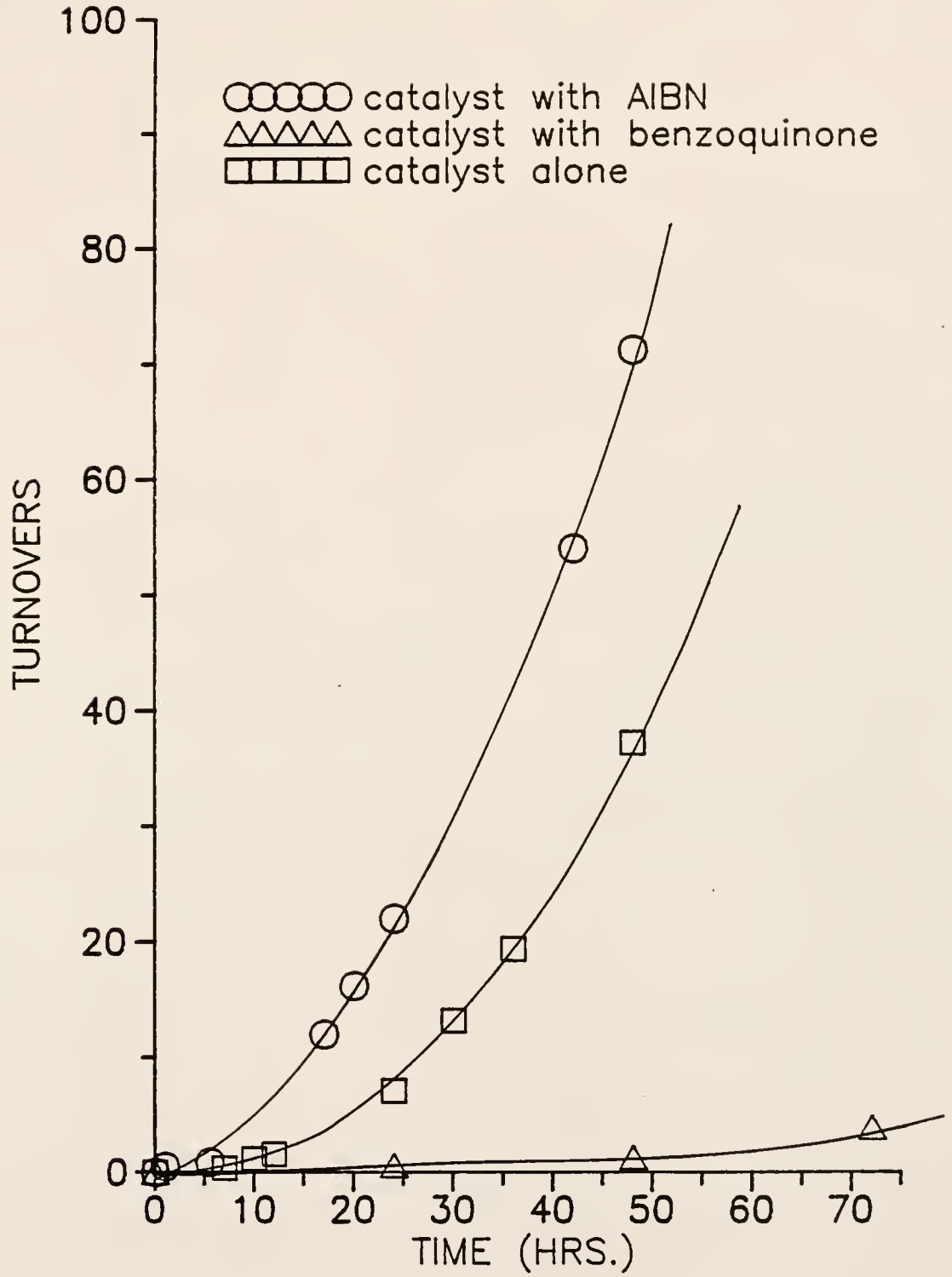


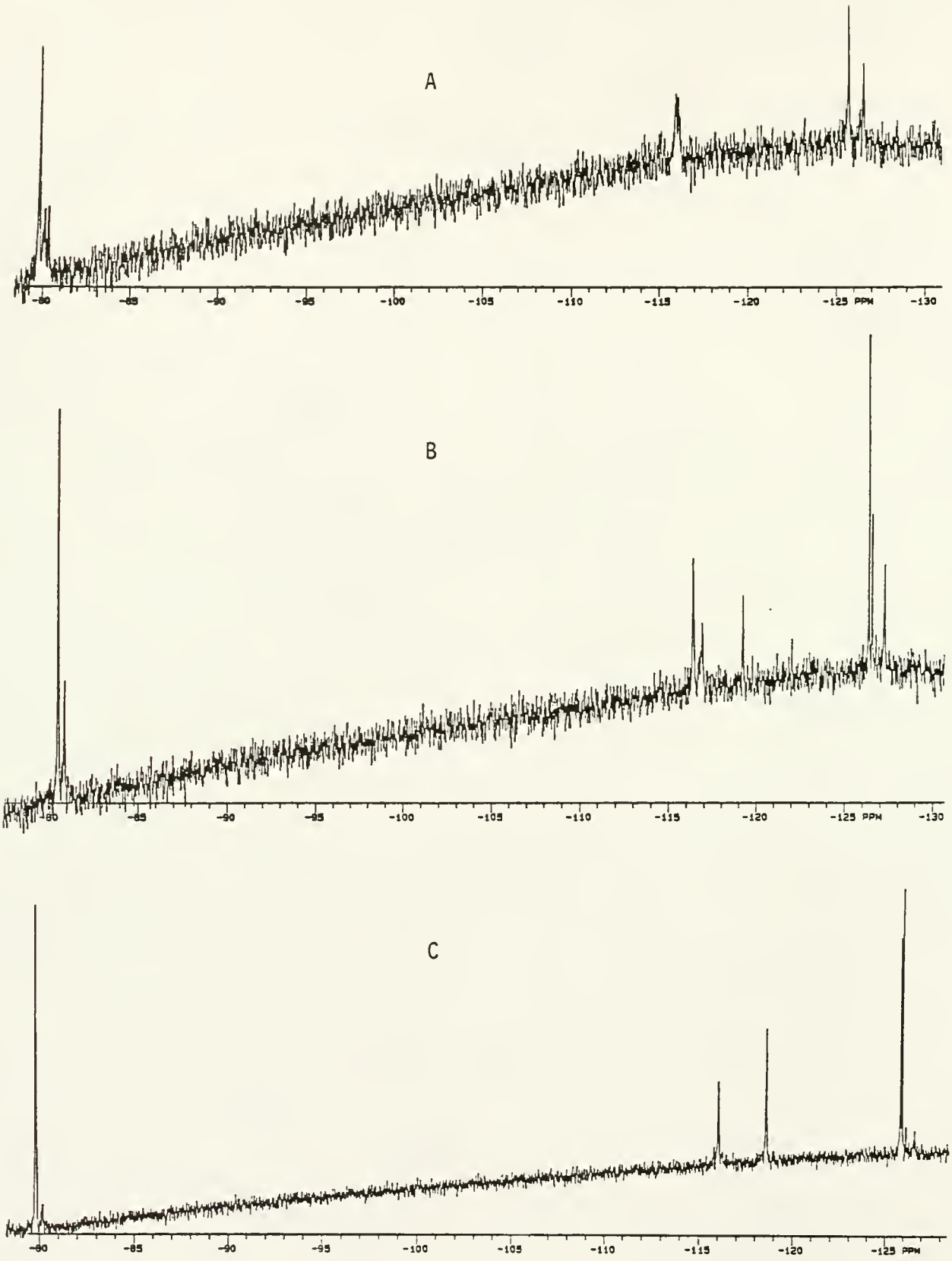
Figure 4.2 Free radical experiments in norbornene oxidations.

the ligands. Any alteration of the catalyst would justify any mechanistic considerations as well.

Several attempts were made to identify the nature of the catalytic species during and after the reaction using norbornene oxidations. The activity of the catalyst levels off after 150 hours of reaction time in a typical norbornene oxidation. Analysis of the spent catalyst indicate the perfluorobutyrate complex decomposes during the reaction. Fluorine NMR of aliquots of actual reaction mixtures taken before the reaction, at the end of the induction period (24 hours), and at 48 hours indicate significant changes in the catalyst are occurring (Figure 4.3) A new resonance at 119 ppm appears after 24 hours of reaction time, while the resonance at 117 begins to disappear. The 117 ppm peak has completely vanished at 48 hours, leaving only the 119 ppm and the original 116 ppm peaks in that region. No integration of these peaks is possible, due to the low concentrations of catalyst (10^{-5} M), the low signal-to-noise ratio, and the baseline roll, an inherent feature of the probe in fluorine NMR. The ν_{CO} stretch in the FTIR shows a similar shift towards the free acid, shifting approximately 20 wavenumbers to higher frequency, from 1704 to 1720 cm^{-1}.

The products observed in the oxidation of these olefins, and the proposed decomposition of the catalyst are consistent with a typical free radical autoxidation mechanism similar to the standard Haber-Weiss scheme mentioned in Chapter I (Figure 4.4). This proposed mechanism involves the one-electron reduction of the catalyst in the presence of an olefin substrate (bound to a Ru

Figure 4.3 ^{19}F NMR of the $[Ru_3O(pfb)_6(Et_2O)_3]^+$ catalyst during norbornene oxidations. (A) catalyst before (t = 0 hours) (B) t = 24 hours (C) t = 48 hours.


A
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125 PPM
-130
B
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125 PPM
-130
C
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125 PPM

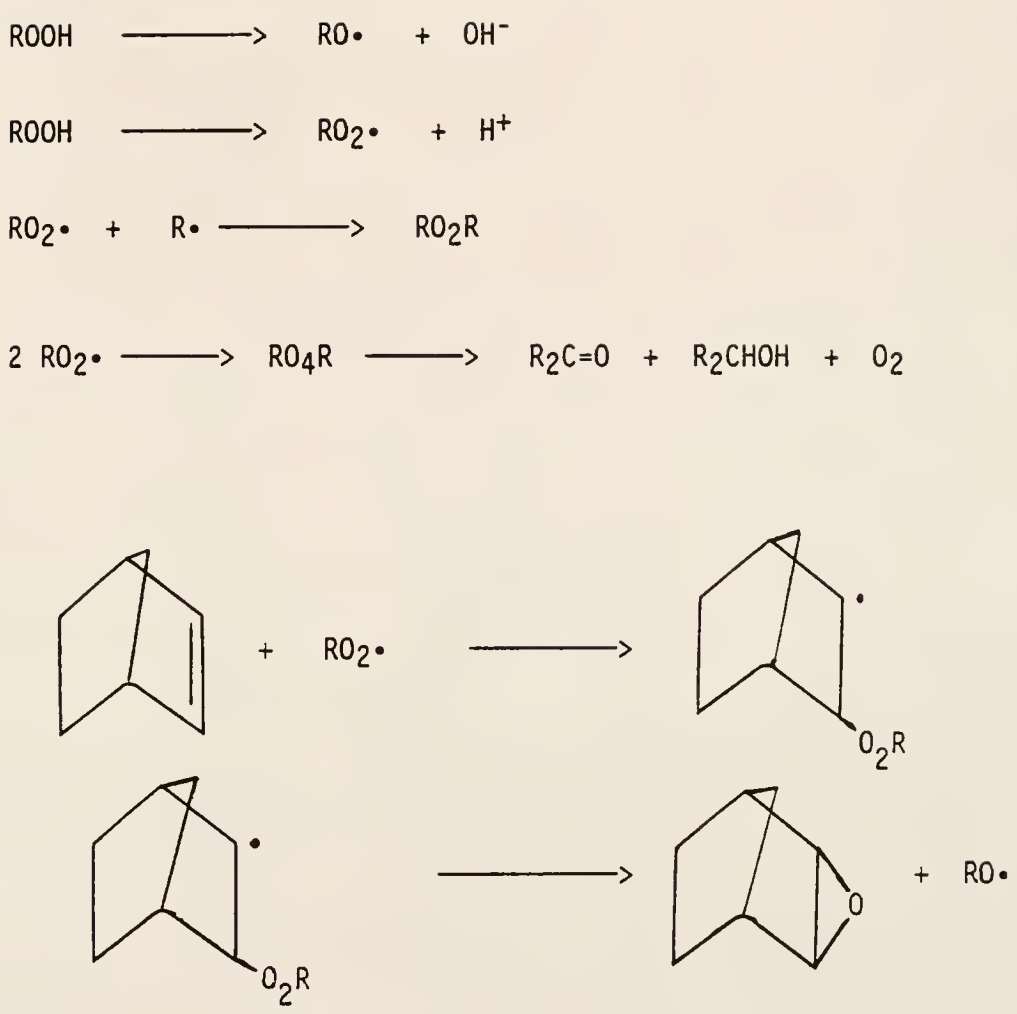


Figure 4.4 Proposed mechanism for the autoxidation of olefins by $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

center) to give an alkyl radical, R• . This radical rapidly reacts with O_2 to give an alkyl hydroperoxide, RO_2• , which can then be decomposed either thermally or by the perfluorobutyrate catalyst to give alcohol and ketone products via a classical autoxidation pathway. A possible route to norbornene epoxide is also outlined in Figure 4.4. This particular route has been previously proposed by Kochi, Lyons and others for the $Co(acac)_3$-catalyzed epoxidation of norbornene.[119] Here hydroperoxy radicals formed thorugh the metal-catalyzed decomposition of hydroperoxides attack the double bond, forming a radical that rearranges to an epoxide.

This mechanism also explains the unreactivity of the alcohol substrates as well. As free radical traps, alcohols would be expected to be inert to free radical initiated oxidations, except under highly stringent conditions. The perfluorobutyrate complex, although an excellent initiator for olefin autoxidations, is not potent enough to initiate the oxidation of alcohols under these conditions.

From the spectral evidence, the catalyst decomposes, indicating the reduction of the catalyst destabilizes the complex in some fashion. The induction period corresponds to the formation of the active catalytic species, which could be a mono- or dinuclear ruthenium species.

Experimental

All reagents used were reagent grade or better. Olefinic substrates were handled as described under "Scope of Catalysis."

The acetonitrile solvent used was HPLC grade and was stored over molecular sieves.

GC analysis was performed as described in Chapter II, using the same DEGS column. All instrumentation used - IR, ^{1}H NMR, and ^{19}F NMR - are the same as described in Chapters II and III. The catalyst was synthesized as described in Chapter III.

CHAPTER V

ALKANE OXIDATIONS BY A NOVEL TRINUCLEAR RUTHENIUM CARBOXYLATE COMPLEX

Introduction

The field of catalysis has grown dramatically over the past 20 years. The challenges of activating H_2, olefins, O_2, CO, and N_2 have all been pursued feverishly by inorganic and organometallic chemists in hopes of discovering unique catalysts or processes to more effectively and selectively utilize these materials. These investigations are further evidence of the cooperativity and interdependence of the fields of homogeneous catalysis and inorganic coordination/organometallic chemistry mentioned in Chapter I. Activation of alkanes, on the other hand, has only recently received similar attention. In 1968, Jack Halpern proclaimed one of the most important and challenging problems in the whole field of homogeneous catalysis was the development of a successful approach to the activation of C-H bonds.[141,142]

The largest scale industrial application of homogeneous catalysis is in the oxidation of hydrocarbons by O_2.[52,143] Primarily, this predomination is due to the control of selectivity afforded by homogeneous processes. As mentioned in Chapter I, the reaction of O_2 with hydrocarbons, although thermodynamically favorable, is hard to initiate, and once initiated, very difficult

to control, so the advantages inherent in homogeneous catalysis are highly desired in industrial alkane oxidations.

Oxidation of hydrocarbons generally involves the formation of an alkyl hydroperoxide which is decomposed into products by a transition metal catalyst (see Figure 1.1). In the majority of the industrial processes to be discussed, the metal complex functions as an agent of decomposition for the alkyl hydroperoxide, and does not interact with O_2 or the substrate.[52] The metal complexes used as catalysts enhance the production of desirable products while also stimulating the production of more radical species to perpetuate the chain.[52]

Two of the most important industrial processes involving the oxidation of hydrocarbons are the production of acetic acid (2.64 billion lbs. in 1984) and adipic acid (1.39 billion lbs. in 1984).[5] Acetic acid is made via the oxidation of butane using a soluble Co(II) salt under highly stringent conditions (Equation 5.1).[52,143]

$$n\text{-}C_4H_{10} \longrightarrow CH_3CC_2H_5 \longrightarrow CH_3COOH \qquad \text{Equation 5.1}$$

(O)

150 - 225 °C
800 psig O_2

93 % yield
45 % selectivity

This process achieved a great deal of its popularity due to the abundance of butane as a feedstock. Newer technology, the carbonylation of methanol by a soluble rhodium carbonyl catalyst, is rapidly taking over as the method of choice for producing acetic acid, however.

The production of adipic acid has been carried out in essentially the same fashion since the 1940's. The commercial process involves the oxidation of cyclohexane to KA oil (a mixture of cyclohexanone (K) and cyclohexanol(A)) by a soluble Co(II) catalyst, again under stringent conditions.[3,52,143,144] The subsequent oxidation of the KA oil in the presence of Cu, O_2, and HNO_3 leads to adipic acid with approximately a 90% yield (Equations 5-2, 5-3).[52]

$$C_6H_{12} \longrightarrow \begin{matrix} C_6H_{11}OH \\ + \\ C_6H_{11}O \end{matrix} \qquad \text{Equation 5-2}$$

$$\begin{matrix} C_6H_{11}OH \\ + \\ C_6H_{11}O \end{matrix} \longrightarrow COOH\text{-}(CH_2)\text{-}COOH \qquad \text{Equation 5-3}$$

The yields of alcohol and ketone range between 60 and 70% in the initial step, but with an incredibly low rate of conversion (10%) for a commercial process.[50,143,144] The process is deliberately kept at such low conversion rates to avoid further oxidation of either the ketone or the alcohol to undesirable products (such as ring-opened acids, alcohols, ketones, and lactones).[145]

Figure 5.1 describes the proposed mechanism for the oxidation of cyclohexane as carried out industrially. In this cycle, the cobalt catalyst is not involved in the reaction of cyclohexane and O_2 to produce cyclohexyl hydroperoxide. The catalyst controls the product distribution (in the absence of any metal ions, the amount

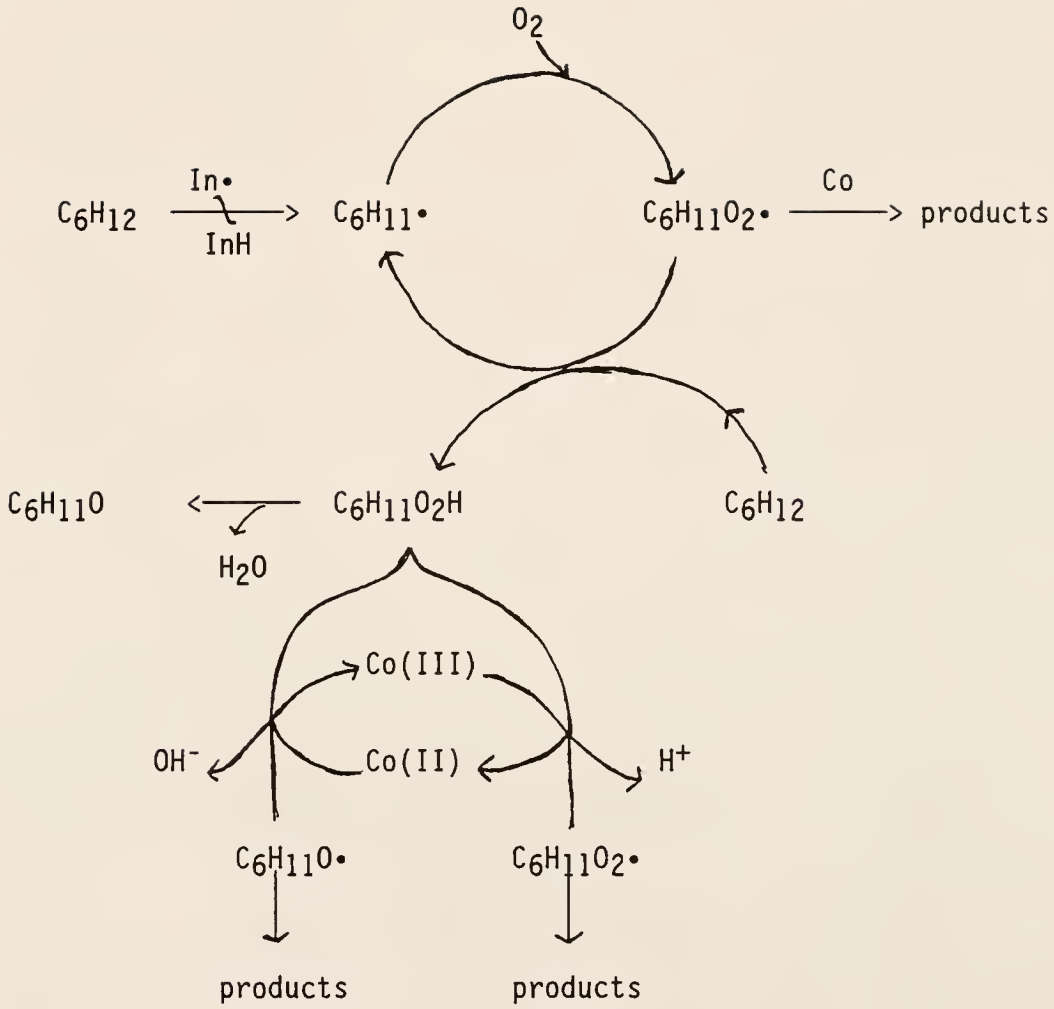


Figure 5.1 Proposed mechanism for industrial cyclohexane oxidations.[6]

of ketone formed is twice that of alcohol) and influences the rate of the reaction in that the metal-catalyzed decomposition of the hydroperoxide generates radicals to continue the reaction.[6,144] However, at high concentrations of catalyst, complexes between the metal ion and the hydroperoxide may form, inhibiting the catalysis to a small degree.[52,146] The actual pathways involved in this reaction are significantly more complex than depicted in this simple diagram.[145]

The academic world has also been interested in the organometallic chemistry involved in the activation of C-H bonds. Initial studies were based on the assumption that the oxidative addition of a C-H bond to a low-valent Group VIII metal should be analogous to the well-studied addition of H_2.[3,142,147] In general, however, saturated hydrocarbons are inert to soluble transition metal complexes. Chloroplatinum complexes (particularly $[PtCl_4]^{2-}$) have been shown to effect the exchange of hydrogen for deuterium atoms in a number of lower alkanes.[142,147-150]

Although this line of research was unsuccessful in producing synthetically useful methods for the activation of alkanes, the recent upsurge of activation mimicking enzymes which are capable of reacting with saturated C-H bonds looks promising. The majority of work in this area has centered around creating a porphyrin analog to the monooxygenase cytochrome P450, as mentioned in Chapter IV. Cytochrome P450 has long been known to hydroxylate alkanes; the mechanism for this reaction involves the Fe(III)-heme center

undergoing a one-electon reduction, binding O_2, and transferring one oxygen atom to a bound substrate and producing one mole of water.[151] Synthetic analogs to this enzyme initially were iron(III) porphyrins, which have been shown to hydroxylate alkanes and epoxidize olefins via an iron-oxo intermediate.[152-155] Metals other than iron as the active site in the porphyrin have also been used in further attempts to create a selective oxidation catalyst. Groves has reported a Cr(III) tetraphenylporphyrin that epoxidizes olefins; the active intermediate in this reaction is presumed to be a Cr(V)-oxo species.[156] Manganese, another metal of biological significance due to its involvement in photosynthesis, has also been studied and shown to transfer oxygen to a variety of organic substrates including alkanes.[157-159] The active species here is again a high-valent metal oxo species, similar to those proposed for the olefin oxidations (see Chapter IV). However, all of these systems use oxygen-atom transfer reagents like iodosobenzene or N-morpholine-N-oxide as the oxygen sources in these reactions rather than molecular oxygen.

Although ruthenium complexes are expected to activate C-H bonds both through direct activation of alkanes and through intramolecular activation of alkyl ligands, studies involving these complexes have been significantly absent.[149] Both Ru(II) and Ru(0) complexes have been shown to catalyze the H/D exchange in alkanes in ligand side chains.[3,9,149] Reversible insertion of the metal into a ligand C-H bond has also been accomplished by a Ru(II) phosphine complex.[160]

In sulfuric acid, both Ru(III) and Ru(IV) will oxidize hydrocarbons, and a combination of Ru(IV)/Cr(VI) will oxidize lower alkanes to alkyl chlorides in aqueous chloride solutions.[52]

High-valent ruthenium-oxo complexes, widely used as catalysts for olefin oxidations (vide supra), have not been successful as hydrocarbon oxidation catalysts. Ruthenium porphyrins have been used to oxidize alkanes with iodosobenzene, but the results are less than spectacular. In methylene chloride solution, the oxidation of cyclohexane produces mostly cyclohexanone and cyclohexyl bromide via a radical process using $Ru(OEP)(PPh_3)Br$ as the catalyst. The mechanism invokes a standard Ru(IV)-oxo species as the active intermediate in this system.[161,162] The ubiquitous ruthenium polypyridyl-oxo complexes will not oxidize alkanes, although these complexes will oxidize water and aromatic hydrocarbons.[163,164]

Taqui Khan has extensively studied the oxidation of cyclohexane using Ru(III)-EDTA complexes.[165-167] These complexes will oxidize a variety of organic substrates, and detailed kinetic and thermodynamic studies of these oxidation have been published. On the basis of these studies, a mechanism involving a μ-peroxo-Ru-cyclohexane adduct is proposed. Cyclohexanol is the primary product; the ketone is formed through the subsequent oxidation of the alcohol. These reactions have also been carried out in the presence of a micelle in a mixed solvent system, and the kinetics of this oxidation studied. The mechanism in this case also involves a peroxo-Ru(IV)-cyclohexane adduct.

The lack of information on the ruthenium-catalyzed oxidation of alkanes combined with the ability of the Ru(pfb) complex to initiate free radical autoxidation prompted the further investigation of the capabilities of this catalyst. The commercial oxidations of alkanes are free radical reactions, so initial studies centered around attempts to oxidize cyclohexane and other alkanes as another test of the versatility of the perfluorobutyrate complex.

Scope of Catalysis

Standard oxidation setups as described in Chapter II were used. Generally, the oxidation reactions were comprised of 40 mL of substrate, 10 mL of acetonitrile solvent, 1 mL benzene standard, and 10^{-5} moles of catalyst. The standard was omitted when it interfered with the analysis of the products in some oxidations. The temperature was maintained at 75 °C by an oil bath, and initial pressures of 40 psig of compressed air were used in all cases. Products were determined by GC using a FID detector and DEGS column. Appropriate calibration curves were constructed and used to quantify the products. In these oxidations, blanks using all reactants except catalyst indicated some reaction occurred after an average of 20 hours of reaction time. For this reason, the length of all alkane oxidations was limited to 12 hours.

Results and Discussion

Although the main substrate of interest was cyclohexane, due to its commercial importance, other alkanes were attempted as substrates as well (Table 5.1). These substrates show strikingly different reactivities. At 75 °C, cyclohexane was oxidized to a

Table 5.1

Alkane Substrates[a]

Substrate	Product	Turnovers/12 hours[b]
cyclohexane	cyclohexanol	15
	cyclohexanone	3
n-hexane	no reaction	
n-hexane[c]	2-hexanol	16
	2-hexanone	16
	1-hexanol	trace
methylcyclohexane	1-methylcyclohexanol	major[d]
	2-methylcyclohexanol	minor[d]
	3-methylcyclohexanol	minor[d]
	2-methylcyclohexanone	trace[d]
3-methylpentane	no reaction	
2-methylpentane	no reaction	
toluene	no reaction	
cyclohexanol	no reaction	

a) All reactions, unless otherwise noted, used acetonitrile (10 mL) as the solvent for the catalyst and 40 mL of substrate. For specific detail concerning reaction conditions, see "Scope of Catalysis."

b) Turnovers = mole of product/mole of catalyst used in the specified time.

c) M-pyrol (or 1-methyl-2-pyrrolidinone) (10 mL) was used as solvent.

d) Not quantified.

mixture of cyclohexanol and cyclohexanone in acetonitrile. N-hexane was unreactive in acetonitrile; in m-pyrol (vide infra) the major products were 2-hexanol and 2-hexanone, with trace amounts of 1-hexanol formed after 12 hours of reaction time. Methylcyclohexane was oxidized to primarily 1-methylcyclohexanol. Smaller amounts of 2- and 3-methylcyclohexanol were also produced, along with trace quantities of 2-methylcyclohexanone. Neither 3-methylpentane nor 2-methylpentane were reactive under these conditions. Cyclohexanol was not oxidized to cyclohexanone, not surprising in light of the results reported in Chapter IV. Under slightly different conditions, refluxing acetic acid (140 °C) with a Br^- promoter in a ground glass apparatus, toluene was not oxidized after 1 hour under a flow of O_2. The change in reaction conditions was warranted by the corrosive nature of the solution.

Of these substrates, cyclohexane was studied the most extensively, in spite of the complexity of the reaction.[145] At 65 °C, the reaction was very slow, forming only trace amounts of products. Raising the temperature to 75 °C increased the rate of the reaction significantly, forming 18 turnovers of total product in 12 hours. Thus, 75 °C was used as the reaction temperature for all subsequent oxidations. Raising the temperature higher is not recommended, since both cyclohexane and acetonitrile boil at 81 °C, and the flammability limits of cyclohexane and air would be exceeded.

The selectivity observed in the oxidation of cyclohexane by the ruthenium perfluorobutyrate catalyst is very high. No traces of

other products are observed in either GCIR or GCMS. Proton NMR of the residue obtained by completely evaporating a standard oxidation shown only small traces of products that could be acids or lactams, leading to the assumption this oxidation occurs with a selectivity for the alcohol and ketone products of 99% or greater.

Work in cyclohexane oxidations has involved the addition of various additives and promoters to enhance product yields, the alcohol/ketone ratio, or suppress undesirable side reactions. The effects of several additives were tested with the pfb catalyst (Table 5.2, Figure 5.2). Bromide ions have long been used as promoters for free radical reactions; Br• species are involved in both initiation and propagation steps in the chain reactions.[52] Under these condition, the addition of bromide enhanced the formation of product; the blanks were inactive. Other transition metals have also been used as cocatalysts in cyclohexane oxidations to influence the product ratios. Chromium(III) enhances the production of ketone and increases the rate of oxidation of cyclohexanol to the ketone.[51] Iron(III) increases the yields of lactone and alcohols and decreases production of acids, while manganese(II) complexes generally increase yields of alcohols and acids.[143] Although the roles of each of these additives in the catalysis is undoubtedly complex, high degrees of variance are possible depending upon the choice of catalysts.

In the ruthenium-catalyzed oxidations, these metals follow these general trends. The addition of $MnCl_2$ increased alcohol production, while $FeCl_3$ increased overall production and increased

Table 5.2

Cyclohexane Oxidation Studies:
Additives[a]

Conditions	Turnovers/12 hours[b] Alcohol	Ketone	Mole ratio Alcohol/Ketone
standard[c]	14.8	3.2	4.6
Mn^{2+}	37.0	9.0	4.1
Br^-	65.1	16.2	4.0
Fe^{3+}	39.7	3.3	12.0
Cr^{3+}	150.3	45.7	3.3
Co^{2+}	--	--	--
$Co(oct)_2$[d]	--	--	--

a) 10^{-5} moles of additive were used in combination with 10^{-5} moles of catalyst. See text for details.

b) Turnovers = mole of product/mole of catalyst in the specified time.

c) Standard conditions are 10^{-5} mole of catalyst. For more detail, see "Scope of Catalysis."

d) Co(II) octoate, DuPont's commercial catalyst, trade name Cobalt Hex-Cem.

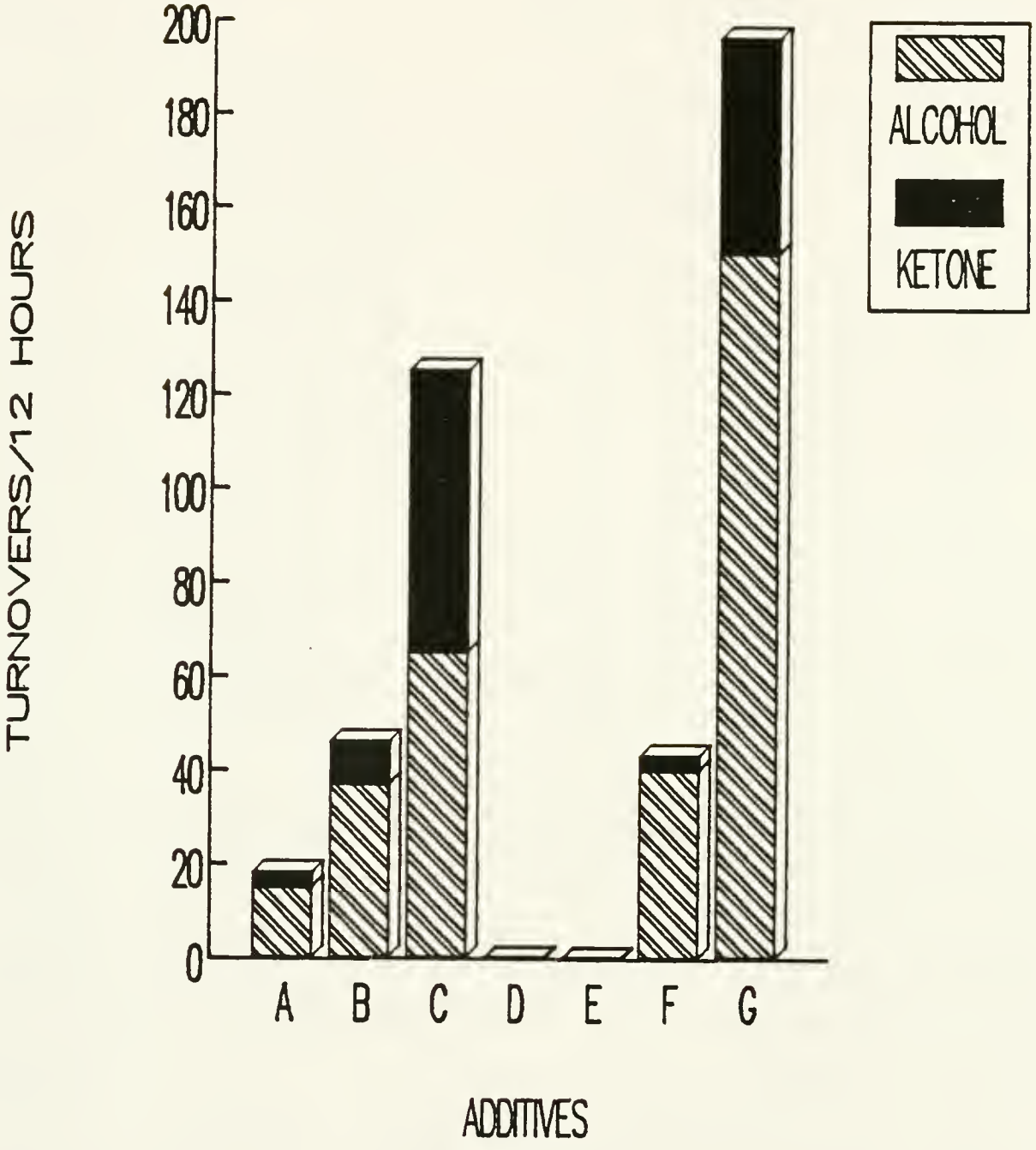


Figure 5.2 Effects of additives in cyclohexane oxidations catalyzed by $[Ru_3O(pfb)_6(Et_2O)_3]^+$. (A) $[Ru_3O(pfb)_6(Et_2O)_3]^+$ (B) $MnCl_2 \cdot 2H_2O$ (C) NaBr (D) $CuCl_2 \cdot H_2O$ (E) $Co(oct)_2$ (F) $FeCl_3 \cdot 6H_2O$ (G) $CrCl_3 \cdot 6H_2O$.

the A/K ratio by a factor of 3. Chromium(III) chloride had a small effect of the A/K ratio while drastically increasing the formation of product by ten-fold. The addition of copper chloride to this reaction completely shut down the reaction. Only a few of these metals show any activity in the blanks. Iron(III) also reacts, producing almost as much product as the iron-ruthenium combination with a similar A/K ratio . Chromium(III) is much less active and produces a 1:1 molar ratio of alcohol to ketone. Interestingly, copper(II) alone is slightly active, producing 3.5 times as much alcohol as ketone. Copper(I) will reduce alkyl hydroperoxides catalytically,[3] but is much less active that the traditional catalysts Mn(II) and Co(II). Since the Cu(II) blank is active, the combination of ruthenium and copper should not have been inactive because both metals will decompose peroxides. Copper is used as the catalyst in the second step in the oxidation of KA oil to adipic acid, so the products formed by the bi-metallic system may have been undetectable under the analysis conditions used.

A sample of the cobalt catalyst used in DuPont's commercial oxidation of cyclohexane was tested under our reaction conditions. This complex, cobalt(II) octoate (or 2-ethylhexanoate), was unreactive at 75 °C, a very encouraging result. Acetonitrile and cyclohexane are only slightly miscible, even at elevated temperature. The biphasic nature of the solution implies that all catalysis is taking place at the interfaces of the micelles that form as the solution is vigorously stirred. In order to draw the

catalyst into the substrate phase, and hopefully enhance the catalysis, sodium octoate [Na(oct)] was attempted as a phase-transfer reagent (Table 5.3). Figure 5.3 illustrates the effects of the addition of various amount of Na(oct) to a typical reaction. More typical phase transfer reagents such as Aliquat 336 are cationic, used for transferring anions from aqueous to organic phases. In this case, transfer of the cationic $[Ru_3O(pfb)_6(Et_2O)_3]^+$ species necessitated the use of an anionic phase transfer reagent. Sodium octoate was chosen for its solubility in cyclohexane and for the use of an anionic carboxylate to replace the perfluorobutyrate counterion. Adding only one-half mole of phase transfer reagent per mole of catalyst increases the reaction rate, but the differences in the amount of product formed with one-half mole and three moles of Na(oct) are insignificant. Also, the solutions are still biphasic, even with four moles of Na(oct) present. Other studies have shown that while Mn(II) stearate will catalyze the oxidation of alkanes, the combination of Mn(II) and potassium stearates is five times more effective.[143] A similar type of synergistic effect may be occurring in these experiments.

The solvent 1-methyl-2-pyrrolidinone (M-pyrol) has been shown to be an excellent medium in which to carry out oxidations.[168] Solvent experiments similar to those in the olefin study were performed for the cyclohexane oxidations (Table 5.4) Several tandem experiments were performed using both m-pyrol and acetonitrile as solvents and varying the ratio of solvent to substrate for each solvent. Under standard conditions (40 mL substrate/10 mL

Table 5.3

Cyclohexane Oxidation Studies:
Phase Transfer Catalysis
by Sodium Octoate

Conditions	Turnovers/12 hours[a] Alcohol	Ketone	Mole ratio Alcohol/Ketone
standard[b]	14.8	3.2	4.6
.5 mole[c]	57.0	13.0	4.5
3 mole	66.0	12.0	5.5
4 mole	27.0	7.0	3.8

a) Turnovers = mole of product/mole of catalyst in the specified time.

b) Standard conditions are 10^{-5} moles of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ catalyst.

c) Amount of Na(oct) per mole of catalyst added to a standard reaction.

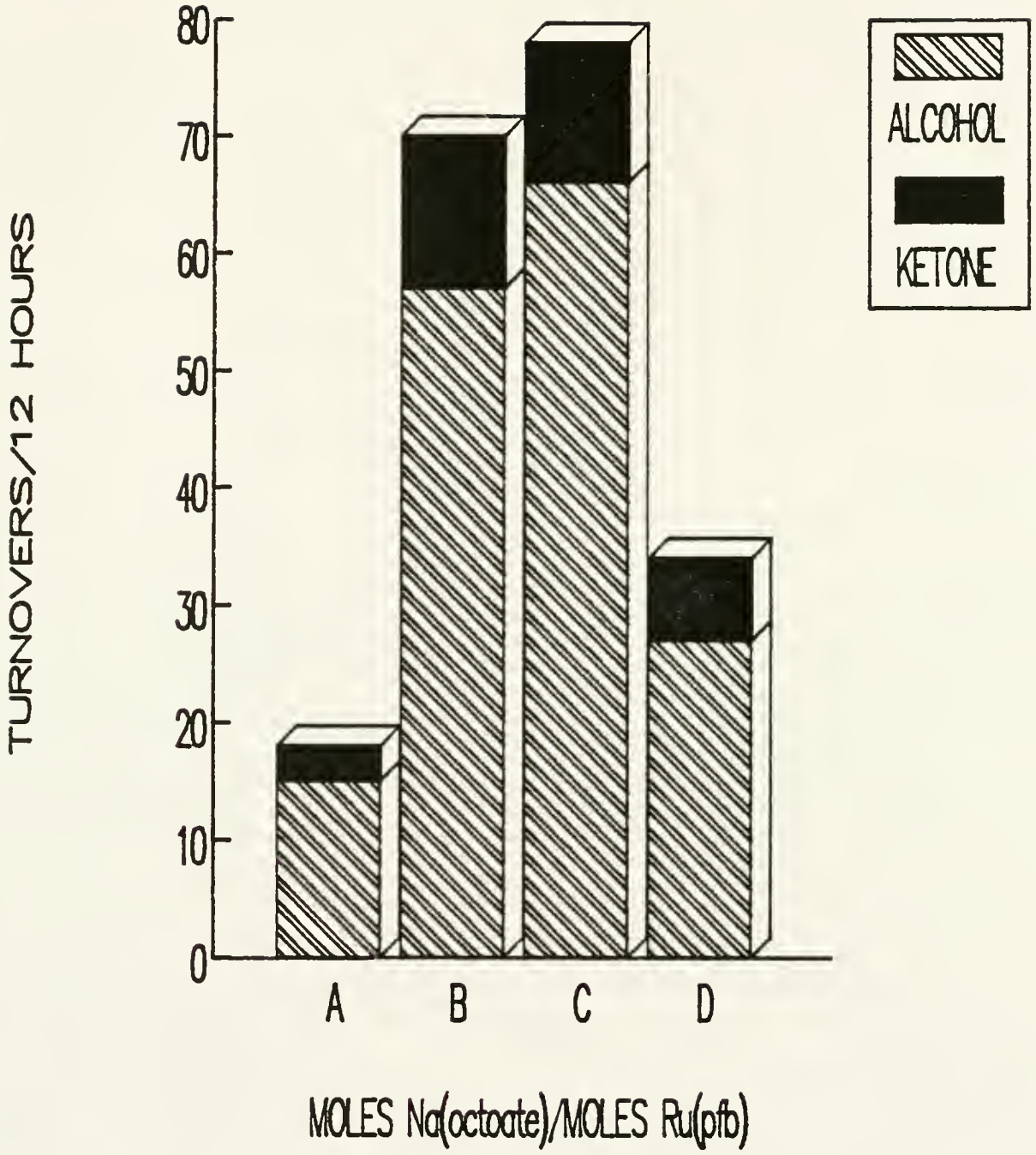


Figure 5.3 Phase transfer in cyclohexane oxidations (A) $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (B) .5 mole Na(oct) (C) 3 moles Na(oct) (D) 4 moles Na(oct).

Table 5.4

Cyclohexane Oxidation Studies:
Solvent Effects

Solvent	Turnovers/12 hours[a] Alcohol	Ketone	Mole ratio Alcohol/Ketone
10 mL MeCN[b]	14.8	3.2	4.6
25 mL MeCN	23.8	6.4	3.7
40 mL MeCN	--	--	--
10 mL m-pyrol[b,c]	20.5	8.9	2.3
25 mL m-pyrol	9.8	2.2	4.4
40 mL m-pyrol	1.6	0.5	3.6
cyclopentanone[c]	--	--	--
cyclopentanone/ MeCN[c,d]	5.2	trace	--
ethanol[c,e]	--	--	--
nitrobenzene[c,e]	--	--	--
DMF[e]	trace	--	--
benzonitrile[e]	4.7	1.6	3.0
pyridine[c,e]	--	--	--

a) Turnovers = mole of product/mole of catalyst in the specified time.

b) The total volume of solvent and substrate was held constant at 50 mL, with the amount of solvent varied as indicated.

c) one phase

d) The mixed solvent system used 5 mL MeCN and 6.5 mL cyclopentanone.

e) All reactions were run under standard conditions using 10 mL solvent.

solvent), little difference is observed for either solvent, except the m-pyrol solution is one phase. Inverting the ratio to 10 mL substrate/40 mL solvent had a considerable effect on the reaction. In 1-methyl-2-pyrrolidinone significantly less activity was observed; in acetonitrile, the catalyst became completely inactive. Changing the ratio to 25/25 increased the reaction in acetonitrile but decreased the reaction in m-pyrol.

Cyclopentanone was attempted as a solvent to solve the phase problem. Industrially, KA oil is used as a solvent to test catalysts, but distinguishing between the solvent added and productformed would be difficult under our conditions. The five-carbon ketone was utilized as the solvent to circumvent this difficulty. The solution was one phase, but no oxidation occurred in 12 hours. A similar reaction was run using 5 mL of acetonitrile as solvent, with enough cyclopentanone added to make the solution one phase. In this mixed solvent system, oxidation of cyclohexane did occur, but the amount of product decreased by one-third. Substituting ethanol for the acetonitrile completely shut down the reaction; interestingly, with alcohol as solvent the reaction mixture was one phase. Catalysis did not occur in either nitrobenzene or pyridine, but in DMF trace amounts of cyclohexanol were found after 12 hours, and the reaction in benzonitrile produced measurable amounts of both alcohol and ketone. These results are strikingly different from those found in the alkene oxidations, where only acetonitrile and ethanol were active solvents.

A plausible explanation involves a major difference in the types of electron transfer involved in these two oxidations. In the olefin oxidations, the substrate is coordinated to one of the ruthenium atoms in the trimer, and inner-sphere electron transfer occurs, forming alkyl radicals and destabilizing the trimer. These radicals initiate the autoxidation chain and the perfluorobutyrate complex decomposes. The solvent variations in the oxidation of cyclohexane indicate a slightly different mechanism is involved. The reaction occurs in relatively polar, moderately coordinating solvents, so that the catalyst should be more properly formulated as $[Ru_3O(pfb)_6(S)_3]^+$ in solution. These coordinating solvents help stabilize the complex during the oxidation, which necessarily occurs via an outer-sphere electron transfer. Alkanes are extremely poor ligands, so it is doubtful that a molecule of cyclohexane is contained in the coordination sphere of the trimer.

If this supposition is true, the possibility arises that the catalyst could remain intact during the oxidation. A slight induction period (approximately 2 hours) is seen in these oxidations, after which the production of alcohol and ketone rises exponentially (Figure 5.4). NMR studies similar to the ones performed on the catalyst <u>in situ</u> for the olefin oxidation were not possible, since the solutions were biphasic. However, ^{19}F NMR of the spent catalyst indicates little change has occurred during the course of the reaction (Figure 5.5). FTIR of the catalyst before and after also shows little change. The stability of the catalyst during the oxidation is more support for a different mechanism than

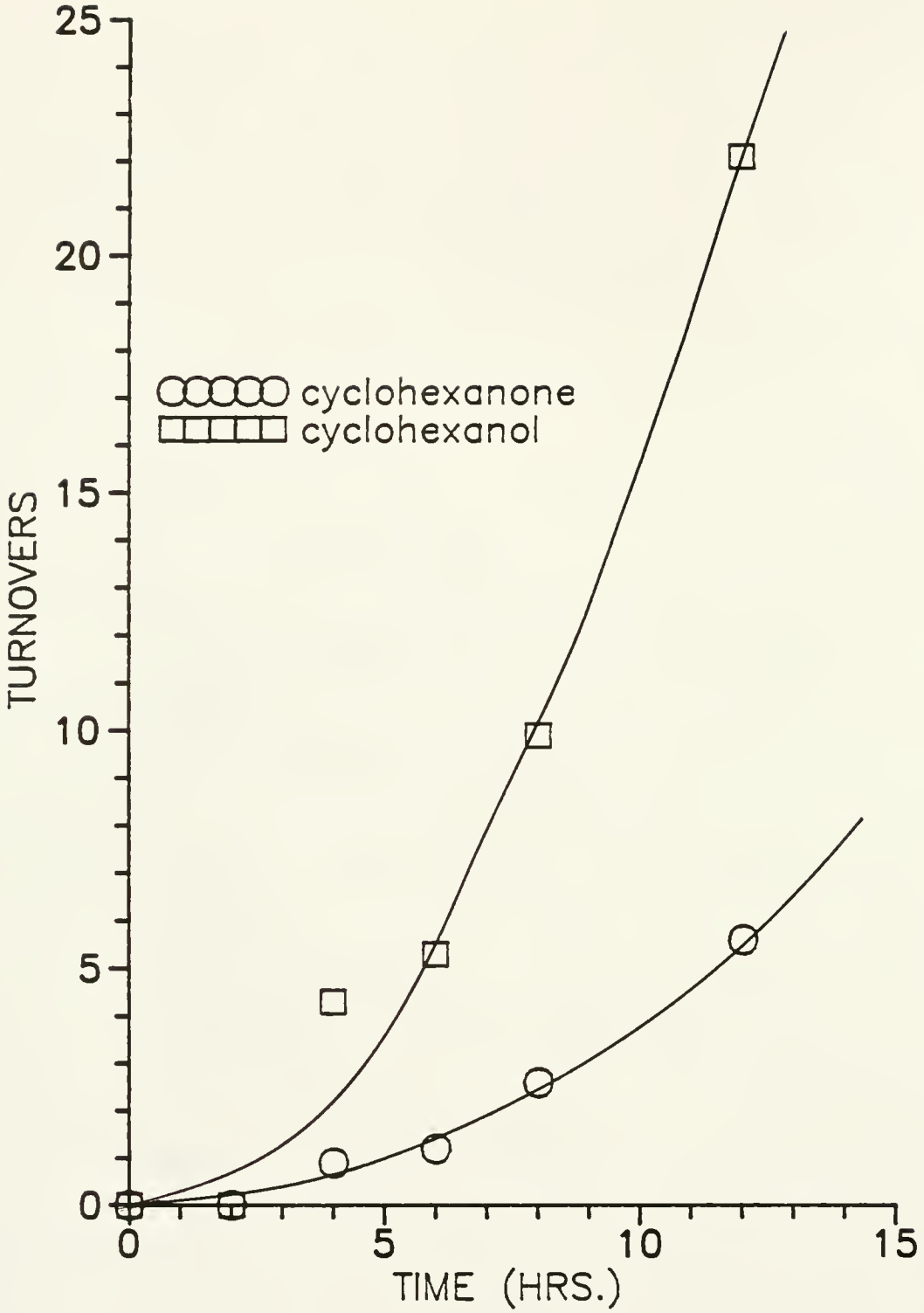
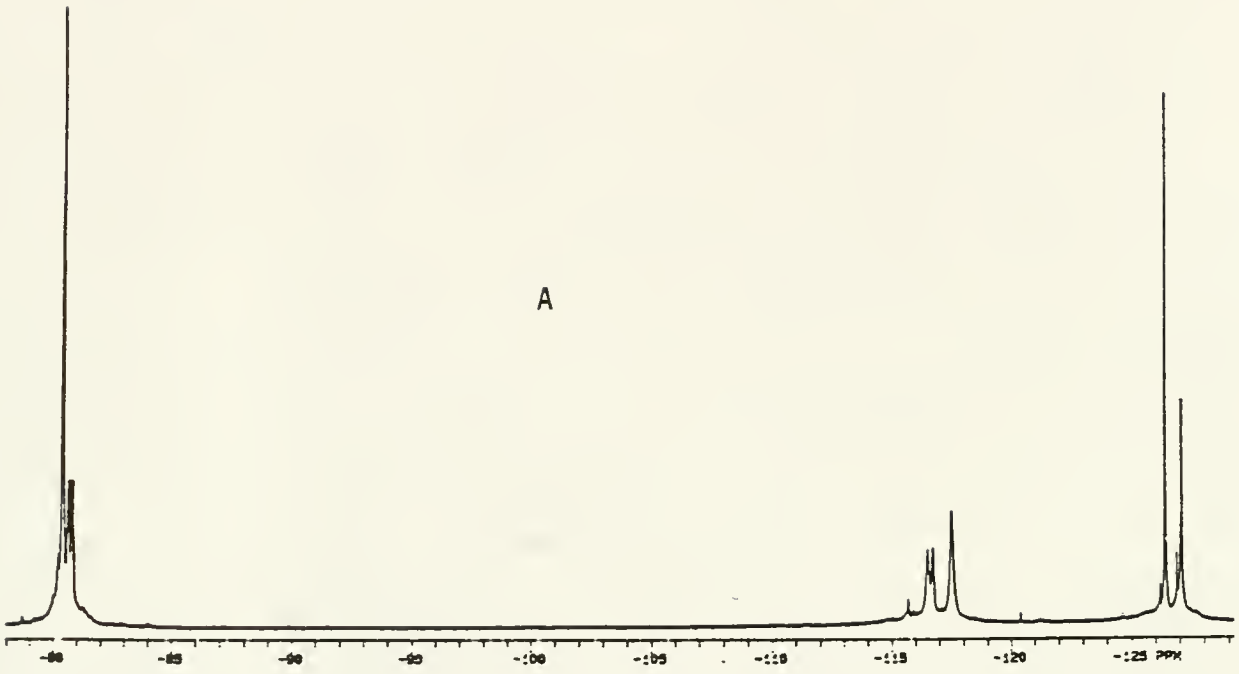
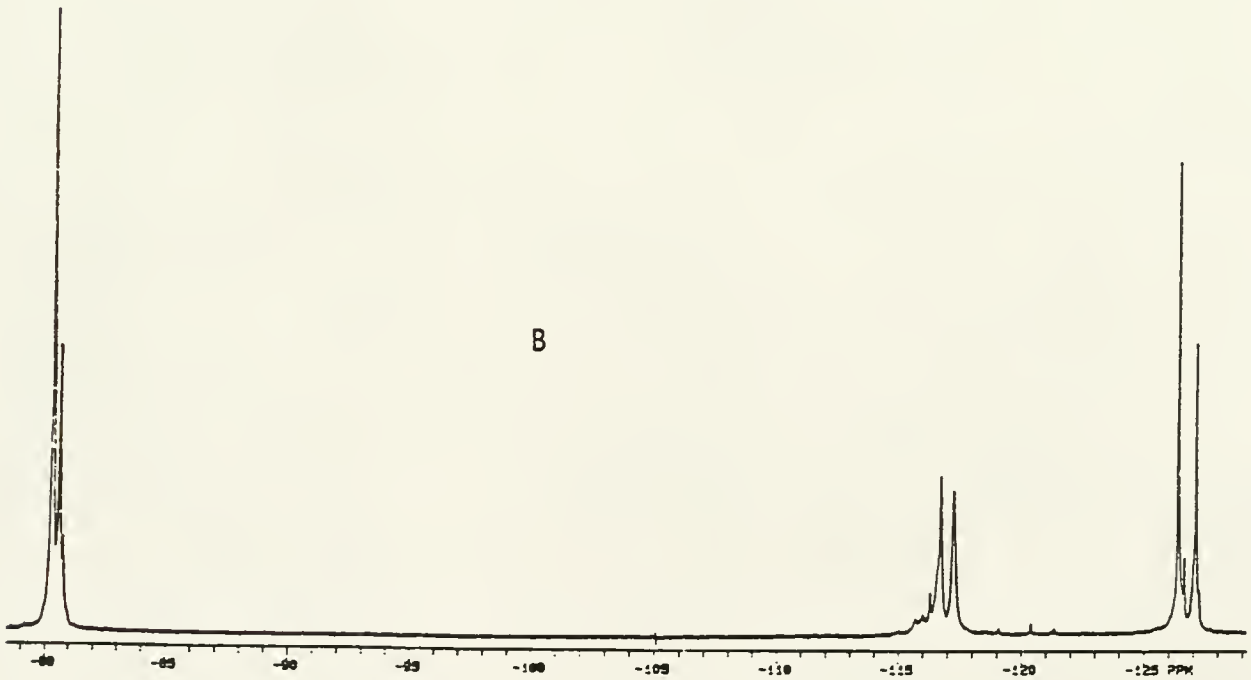


Figure 5.4 Activity curve for the oxidation of cyclohexane by $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

Figure 5.5 ^{19}F NMR of $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ during cyclohexane oxidations (A) before catalysis (B) after 12 hours of reaction time.


A
-125 PPM


B
-125 PPM

that involved in the olefin oxidations, where the catalyst decomposes.

Standard free radical experiments were performed in these oxidations as well (Figure 5.6). The addition of benzoquinone to the reaction decreased the amount of product formed by one-third (from 28 turnovers of total product to 16). The addition of AIBN to a standard reaction had no effect at all. Using AIBN alone (with no ruthenium catalyst) did not initiate the reaction, only achieving .8 turnovers of total product. These experiments indicate the reaction involves free radicals, and the ruthenium perfluorobutyrate complex is a more potent initiator than AIBN in this biphasic system.

Since free radicals are involved, more than likely peroxides or hydroperoxides are formed as intermediates as well. Sharpless[112] has published a method for titrating peroxides in organic solvents that has proven to be useful in other biphasic catalyst systems studied.[169] For these peroxide titrations, several modifi-cations of the original procedure were necessary. A larger aliquot of analyte (10 mL) was used, and the solutions were not diluted with 100 mL of water. The peroxide concentrations were very low, so larger aliquots and no dilution was necessary; the water also formed an emulsion with the cyclohexane, making the endpoint of the titration very difficult to see. The titrant was diluted from .10 N to .001 N to obtain reasonable values for the volume of titrant required. Two different blanks were run, one with all components of a standard oxidation without catalyst stirred at room temperature for 30 minutes, and one under pressure for 12 hours. A standard

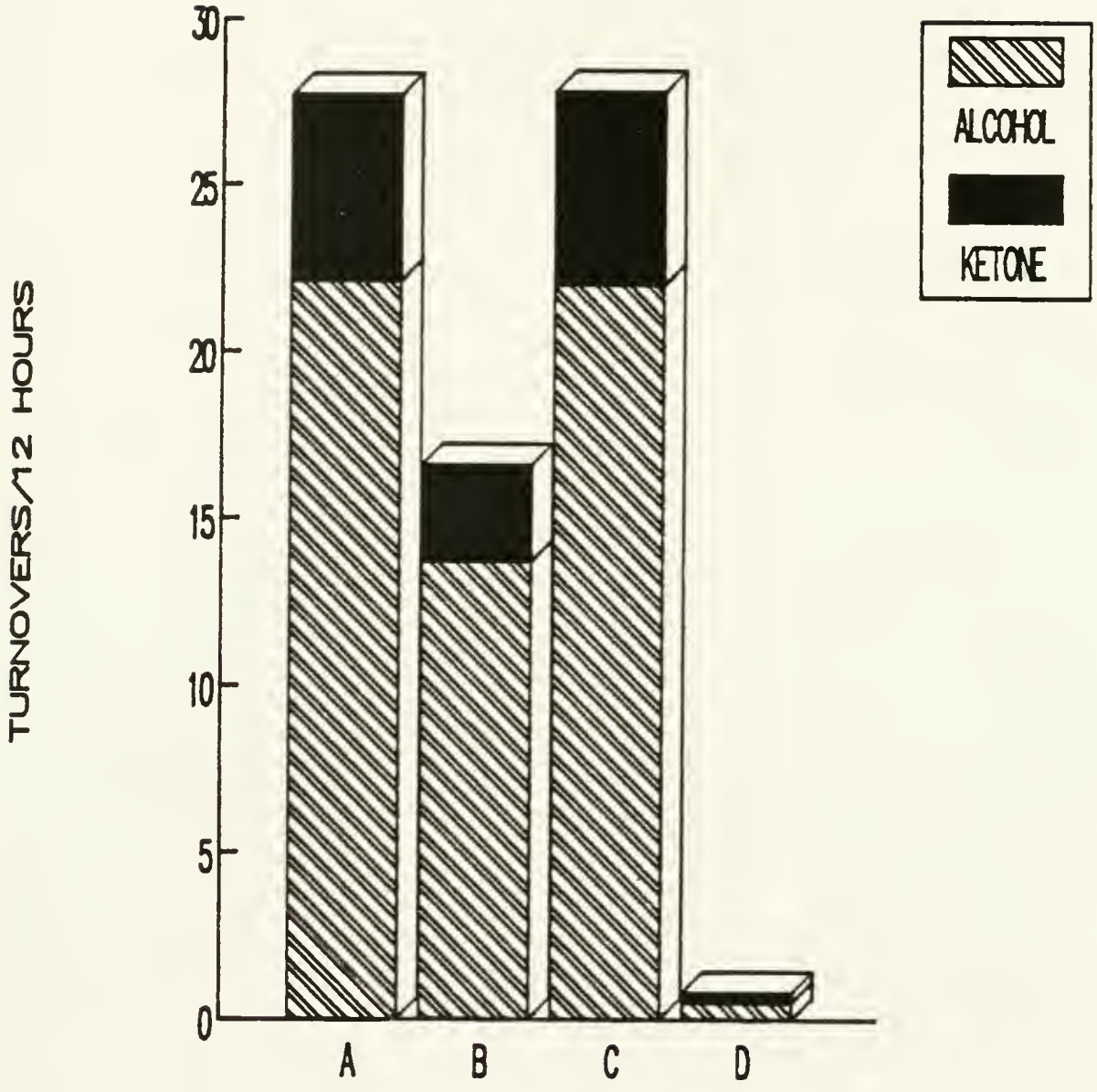


Figure 5.6 Free radical experiments in cyclohexane oxidations. (A) $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (B) catalyst and benzoquinone (C) catalyst and AIBN (D) AIBN alone.

oxidation including catalyst was also set up for 12 hours. The solvents already contain a small amount of peroxides (7.0×10^{-6} N), and the blank under pressure titrated for two orders of magnitude more (1.2×10^{-4} N). Titrating the catalyst run was a challenge since the greenish solution were to be titrated from yellow to colorless. A larger amount of error is present in the titrations of the catalyst, but this reaction contained the most peroxide (8.65×10^{-4} N), as would be expected. However, these small differences in peroxide concentration between the catalyst and blanks do not account for the large amount of product formed. The method is suspect, especially at such low concentrations, but an additional factor to consider is that the decomposition of peroxides in solution continues in the presence of the catalyst, even after removal from heat and pressure, making the amount of peroxide in the standard catalyst solution lower than it should be. However, these experiments do indicate more peroxides are formed in the presence of the ruthenium perfluorobutyrate catalyst.

The mechanism proposed for these oxidations is slightly different than that for the industrial-scale oxidations (Figure 5.7). The catalyst, solvated by a coordinating solvent, forms an outer-sphere complex with the substrate. Electron-transfer from the Ru_3O core to the alkane forms an alkyl radical, which rapidly reacts with O_2 beginning the chain reaction, and a reduced form of the trimer. The catalyst is probably involved in the decomposition of the alkyl hydroperoxides after they are formed as well. By analogy with the alkyl carboxylate trimers, the reduced ruthenium trimer is

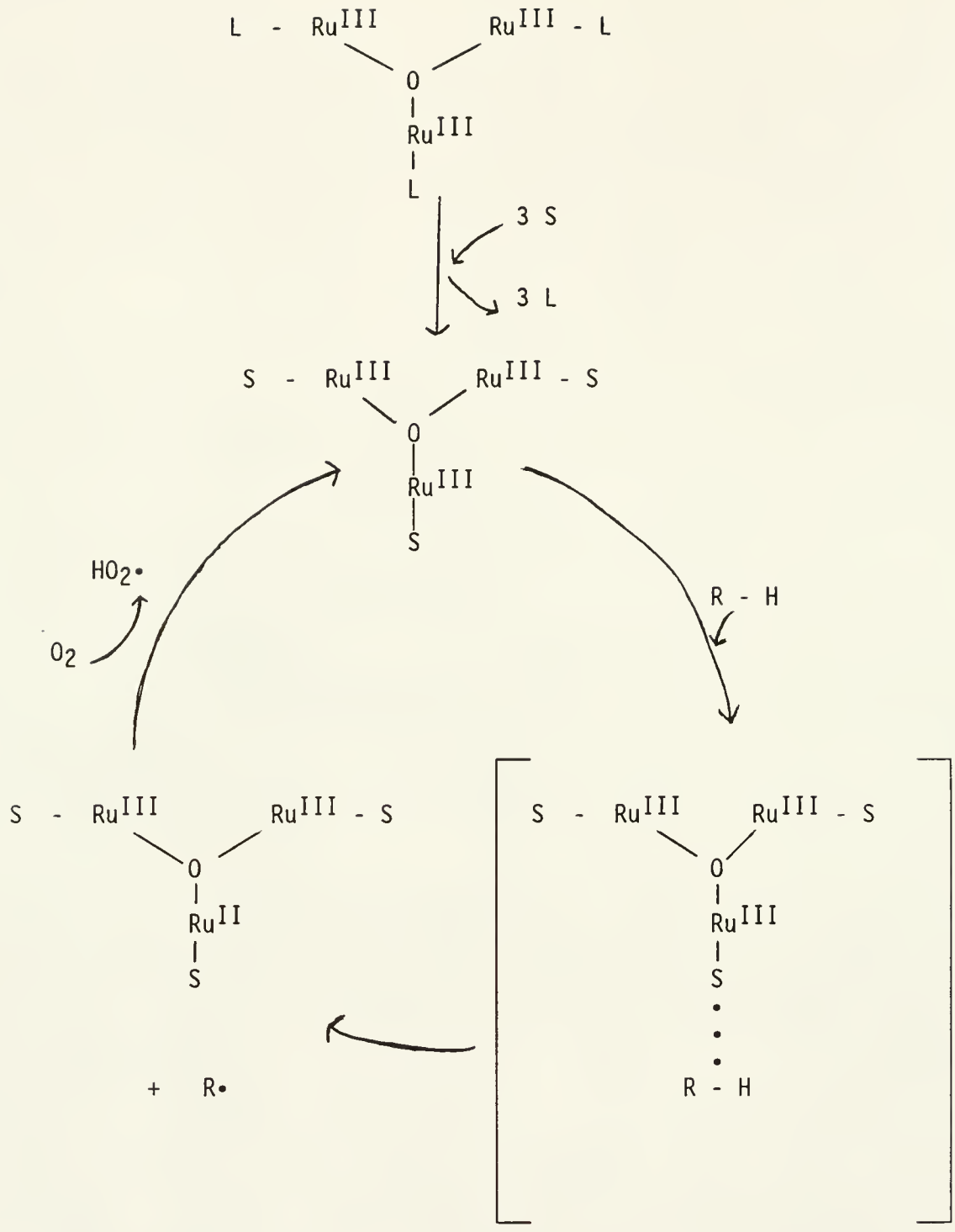


Figure 5.7 Proposed mechanism for alkane oxidations by $Ru_3O(pfb)_6(Et_2O)_3^+$.

rapidly oxidized back to a Ru(III,III,III) species by O_2, regenerating the active catalyst.

Experimental

All reagents used were of the best quality available. Cyclohexane (Spectranalyzed) and benzene (SpectrAR) were used as received; HPLC grade acetonitrile was stored over activated molecular sieves. Hexane was purified by stirring for several hours with H_2SO_4, washing with water several times, and drying over $CaCl_2$.[170] Before use, the hexane was passed through a column of neutral alumina. No purification was necessary for any other substrates used. Du Pont's catalyst, Co(octoate), trade name Cobalt Hex-Cem at 12% cobalt was donated by Mooney Chemical Company.

All equipment was described in Chapter II. The catalyst was prepared as described in Chapter III. All instruments used (FTIR, NMR) are as described in Chapters II, III, or IV.

CHAPTER VI

CONCLUSIONS

The series of trinuclear ruthenium carboxylate complexes has fulfilled its promise of highly intriguing chemistry. The catalytic potential of these compounds, tapped essentially only in the area of reductions, has been explored further, primarily in the area of oxidations. The use of molecular oxygen as the primary oxidant, in combination with these complexes, has made these inquiries even more unique. A wide variety of ruthenium carboxylate complexes were investigated as catalysts for the oxidation of essentially the entire range of organic substrates.

Trinuclear ruthenium carboxylates of the formula $[Ru_3O(O_2CR)_6(L)_3]^{n+}$ where R = CH_3, C_2H_5; L = H_2O, PPh_3, py; n = +1, 0, selectively oxidize primary alcohols to aldehydes and secondary alcohols to ketones in the presence of molecular oxygen. The proposed mechanism for these oxidations involves a Ru(II)-Ru(IV) cycle that assumes retention of the trimeric structure. However, these complexes are unable to oxidize olefins.

A novel member of this series, a trinuclear ruthenium carboxylate containing completely fluorinated carboxylate ligands, has been synthesized and characterized. The exchange of alkyl for fluorinated carboxylates was based on the assumption the electron-

withdrawing character of the fluorinated ligand would increase the acidity of the metal, making it more likely to bind olefins, as well as making the Ru(III) centers better oxidants. Without a crystal structure, the exact nature of this complex cannot be definitively identified; however, the experimental evidence leads to the formulation of this novel complex as $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$.

This novel complex was screened as a catalyst for the oxidation of olefins by O_2. The goal of synthesizing a catalyst, i.e., the ruthenium perfluorobutyrate complex, that would selectively oxidize olefins to the epoxide was not realized. This catalyst initiated the free radical autoxidation of all of the alkene substrates attempted. Spectral evidence indicated the decomposition of the catalyst, probably to a mono- or dinuclear ruthenium species. The mechanism for this reaction involves a standard Haber-Weiss decomposition of alkyl hydroperoxides by the catalyst, forming products, with subsequent decomposition of the trimeric catalyst.

Other substrates were screened with the perfluorobutyrate complex as well. Alkanes, the most difficult substrates to oxidize, were successfully converted to oxygenated products by this complex and molecular oxygen. Interestingly, this complex will oxidize cyclohexane to a mixture of cyclohexanol and cyclohexanone under conditions significantly less strenuous than those used in industry. The mechanism for this reaction is decidedly different from the typical free radical mechanism proposed for the olefin oxidations. No decomposition of the catalyst occurs, and the cluster seems to

remain intact during the production of cyclohexyl radicals and the subsequent decomposition of the peroxides formed form this radical.

The successes of these complexes as catalysts lead to speculation about the catalytic potential hidden in other trinuclear carboxylate complexes. Most intriguing in light of current interests in mixed-metal catalysis is the possibility of mixing different metals in the M_3O core. Such a catalyst theoretically could be designed and "tuned" to achieve selective activation of substrates by the judicious choice of metals placed in the trimer. Further investigations of the catalytic potential of this family of compounds is warranted based on these studies of the ruthenium system.

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BIOGRAPHICAL SKETCH

Shannon Davis, born December 6, 1963, lived for most of her formative years in the town of her birth, Statesboro, Georgia, except for a sojourn of two years in Athens, Georgia. As a senior in high school, part of a joint enrollment program, she entered Georgia Southern College in 1980. She majored in chemistry, and after a short stint as a lab technician at Braswell Food Company (determining the pH of pickles and the sugar content of jams and jellies) she became firmly committed to pursuing the science in graduate school. She graduated from GSC in June of 1984 with the degree B. S. in Chemistry, and the following August she moved to Gainesville and began her graduate career at the University of Florida. After a brief stay of four years, she expects to receive her Ph.D. in inorganic chemistry officially in December 1988. In the fall of 1988, she will move to Pensacola, Florida, where she will join the Fiber Intermediates Division of Monsanto Chemical Company.

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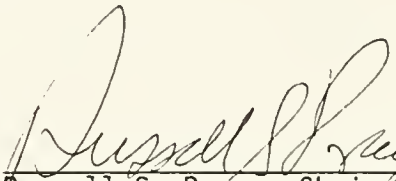

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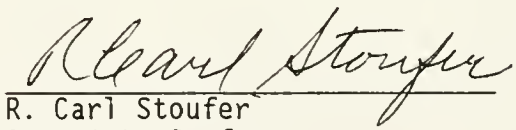

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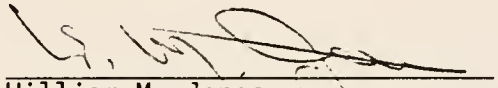

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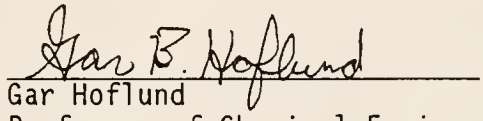

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1988

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